Analytical Abstracts

A monthly publication dealing with all branches of analytical chemistry: issued by the Society for Analytical Chemistry

Volume 8
No. 6, Abstracts 2264-2731

June, 1961

Published for the Society by
W. HEFFER & SONS LTD., CAMBRIDGE, ENGLAND

Binding . . .

W. Heffer & Sons Ltd. announce that they are now able to BIND copies of ANALYTICAL ABSTRACTS, in an approved binding case, at a cost of 14/6 per volume. The 12 Parts for 1960 together with Index and remittance for 14/6 should be sent to

W. HEFFER & SONS, LIMITED
HILLS ROAD, CAMBRIDGE

IMPORTANT NOTICE TO SUBSCRIBERS

(Other than Members of the Society)

The Subscription to *Analytical Abstracts*, inclusive of Index, is £5 per annum; and for *Analytical Abstracts* together with *The Analyst* and Indexes is £8 8s. per annum.

The price of single copies of *Analytical Abstracts*, including back numbers, is 10s. 6d. post free.

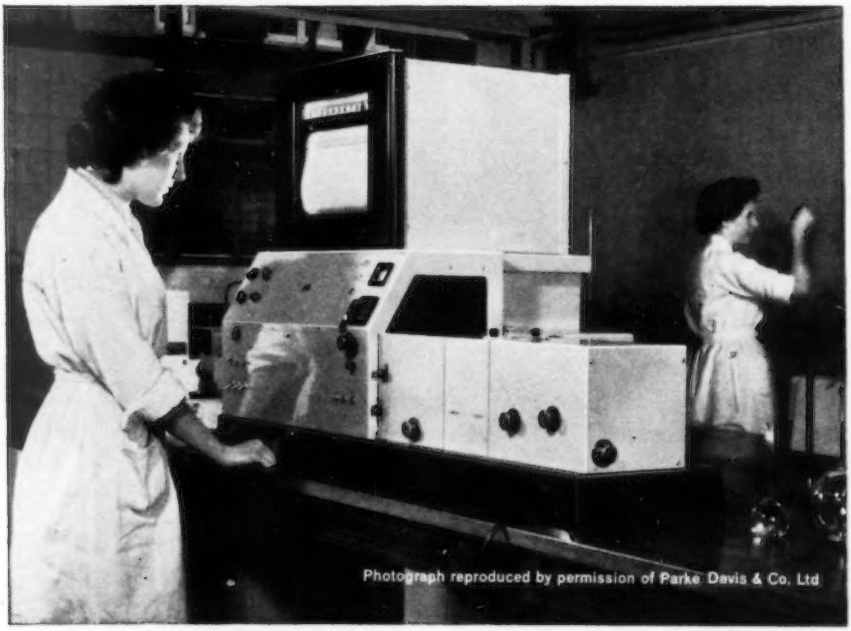
Analytical Abstracts is available printed on one side of the paper only, suitable for incorporation into reference systems; the cost is £5 7s. 6d. per annum, exclusive of Index.

All further enquiries about subscriptions should be made through the Secretary, the Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1. Telephone: BELgravia 3258.

UNICAM

This is the SP.700 Spectrophotometer. One of the most advanced analytical instruments of its kind. Precise — versatile — reliable — made for analysis through a spectral range of Ultraviolet, Visible and Near Infrared. The SP.700 records a detail of the composition of unknown mixtures — detects minute traces of the most elusive elements — completes in minutes a task which would take hours or weeks by other methods.
Used by scientists in the great University and Industrial Laboratories of the world. Made by Unicam Instruments Ltd., Cambridge, England.

SP.700 Recording Spectrophotometer



UNICAM INSTRUMENTS LIMITED · CAMBRIDGE · ENGLAND
U.I.

Over 5,000 chemicals for science

THE H & W RANGE is comprehensive and up-to-date. Everyday needs of research and analysis are covered by **'ANALAR'** and **G.P.R.** (General Purpose Reagent) Chemicals.

The following are selected titles from 23 special purpose ranges detailed in our 1960 Catalogue—

Organic Reagents for Metals
'P.V.S.' Reagents—Purified for Volumetric Standardisation.
'M.F.C.' Materials for Chromatography.
'Spectrosol' Solvents—to meet the special requirements of absorption spectroscopy.
Metal Indicators for complexometric titrations.
'REVECTOR' Microscopical Stains.

Technical literature is available on many of these specialities.

H & W

FINE CHEMICALS

for research, analysis and industry

HOPKIN & WILLIAMS LTD., CHADWELL HEATH, ESSEX, ENGLAND

Branches: London, Manchester, Glasgow *Agents throughout the U.K. and all over the world*

TAS/HW.11

ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

2264. **Annual review, 1960.** *Japan Analyst*, 180 pp. The following review articles are included, all in Japanese. **The present situation of analytical chemistry,** T. Takahashi, 1–2. **Emission spectroscopy,** K. Nagashima and T. Nakajima, 3–10. **Infra-red and Raman spectroscopy,** N. Ooi, 10–16. **X-ray analysis,** T. Kubo and S. Kato, 16–19. **Mass spectrometry,** T. Tsuchiya, A. Hashizume and K. Someno, 19–22. **Nuclear magnetic resonance spectroscopy,** S. Fujiwara, 23–26. **Ion exchange,** H. Kakihana, H. Tsubota and A. Tsuji, 26–33. **Chromatography,** K. Satake, T. Seki, S. Harasawa, T. Muto and M. Maruyama, 34–52. **Organic electrophoresis,** K. Shimao and H. Hirai, 53–55. **Solvent extraction,** T. Kiba, 55–61. **Organic elementary analysis,** T. Mitsui, 62–66. **Organic qualitative analysis,** T. Momose, 66–70. **Microbioassay,** K. Sugimura, 70–74. **Water analysis,** K. Sugawara, T. Kato and T. Sawaya, 75–85. **Iron and steel,** H. Goto and S. Suzuki, 85–94. **Polymers,** Y. Takayama, 94–98. **Essential oils,** T. Mitsui and W. Tagaki, 98–101. **Surface-active agents,** Y. Izawa and W. Kimura, 101–104. **Biochemistry,** Y. Matsumura, M. Saito, M. Kitamura, S. Kawamura and I. Hara, 105–128. **Food,** T. Obara and Y. Ogasawara, 129–132.

2265. **Analysis for industry.** W. I. Stephen. *Ind. Chem.*, 1960, **36** (8), 408–410; (9), 459–461.—Specialised methods and techniques are discussed with special reference to the fundamental principles and qualitative applications of the ring-oven method to microchemical separations. The use of this technique in electrographic analysis, in solvent extraction procedures and in the identification of radioactive substances is discussed. (20 references.)
S.C.I. ABSTR.

2266. **Determination of errors in chemical analysis.** M. Beneš and K. Eckschlager (Inst. Res. Ores, Prague). *Chem. Listy*, 1960, **54** (10), 1089–1114.—A survey of statistical methods is presented, with 65 references. J. ZÝKA

2267. **Errors in chemical analysis.** K. Eckschlager (Inst. Res. Ores, Prague). *Chem. Průmysl*, 1960, **10** (11), 585–587.—Errors of weighing or measurement of the vol. of the sample with pipette or burette are tabulated and mathematically evaluated.
J. ZÝKA

2268. **Errors in gravimetric analysis.** K. Eckschlager (Inst. Res. Ores, Prague). *Chem. Listy*, 1960, **54** (11), 1133–1143.—A survey is presented, with 36 references. J. ZÝKA

2269. **Combined estimates in colorimetric determinations with high variability.** P. A. Anastassiadis (Dept. of Agric. Chem., Fac. of Agric., McGill Univ., Macdonald College, Quebec). *Canad. J. Biochem. Physiol.*, 1960, **38** (11), 1223–1227.—The precision of colorimetric determinations made against standards depends on the variability of observations made on the sample and those made on the standard. The total variability is made up of that which occurs on repetition at different times (inter-variance) and that which occurs between replicates done simultaneously (intra-variance). Practical considerations limit the number of observations on the sample, but with time a mounting number of observations on the standard accumulates. In any determination two estimates of the sample can be obtained, one by using the observations on the standard done simultaneously with the sample and the other by using the cumulative pooled observations on the standard. By using a weighted average of these two the precision of the estimate is much increased. Formulae and tables are given for the calculations and the method is exemplified by 16 separate estimations on separate days, in duplicate, of hexosamine (presumably) in a sample of tissue. The estimates on the individual days, taking only the observations of the day, ranged from 2·93 to 4·85 μg per g with a mean of 3·71 and a standard deviation of 0·418; taking the individual day observations for the sample and pooled observations for the standard, the corresponding figures were 3·16 to 4·45, 3·72 and 0·542; by using weighted averages of the individual day for the sample and cumulative data for the standard, the figures were 3·18 to 4·52, 3·68 and 0·331. J. I. M. JONES

2270. **Third Conference—Analytical Chemistry in Nuclear Reactor Technology. Analysis of Reactor Fuels, Fission-product Mixtures and Related Materials. Analytical Chemistry of Plutonium and the Transplutonic Elements. Oct. 26 to 29, 1959. Gatlinburg, Tenn.** *Talanta*, 1960, **6** (Special number), 276 pp. The following papers, not published elsewhere, are included. **Standards in the nuclear energy programme,** C. J. Rodden, 3–19. **The high-radiation-level analytical facility at the Oak Ridge National Laboratory,** C. E. Lamb, 20–27. **Determination of iron in yttrium,** J. O. Hibbits, W. F. Davis and M. R. Menke, 28–29. **Some applications of high-frequency titrimetry,** D. L. Manning and O. Menis, 30–41. **X-ray absorption edge analysis,** H. W. Dunn, 42–45. **X-ray fluorescence spectrographic determination of impurities and alloying elements in tantalum container materials,** E. A. Hakkila and G. R. Waterbury, 46–51. **Analysis of a liquid metal reactor fuel,** L. Newman, T. Prach and H. L. Finston, 55–62. **Method of uranium isotope analysis by direct-reading emission spectroscopy,** J. L. Saunderson, 63–70. **Spectrochemical analysis of bismuth using a photo-electric spectrometer,** J. Forrest and H. L. Finston, 71 (summary only). **Determination of uranium-235 burn-up in irradiated**

natural uranium by chemical and counting methods, D. R. MacKenzie, 72–93. **Analytical methods used in a study of reactivity changes with long irradiations,** R. G. Hart, C. B. Bigham and M. Lounsbury, 94–99. **Colorimetric determination of zirconium in plutonium - uranium - "fissium" alloys,** R. F. Buchanan, J. P. Hughes and C. A. A. Bloomquist, 100–104. **Analytical programme for processing stainless steel - uranium dioxide reactor fuel elements,** G. A. Huff, 105–111. **Simplified method for radio-iodine analysis,** H. M. Eiland, 112–116. **Radiochemical analysis of reactor effluent waste materials at Hanford,** R. W. Perkins, 117–132. **Radiochemical analysis of corrosion product mixtures from high-temperature pressurised water loop systems,** L. C. Bogar and C. J. L. Lock, 133–143. **Analytical laboratories for the handling of plutonium,** C. F. Metz and G. R. Waterbury, 149–153. **The high-alpha-radiation analytical facility of the Oak Ridge National Laboratory,** J. H. Cooper, 154–158. **Determination of plutonium based on National Bureau of Standards potassium dichromate,** C. E. Pietri and J. A. Baglio, 159–166. **Determination of americium in plutonium alloy fuels for fast reactors,** J. Bubernak, M. Lew and G. Matlack, 167–172. **Determination of nitrogen, americium, neptunium and uranium in p.p.m. quantities in pure plutonium,** R. F. Buchanan, J. P. Hughes, J. J. Hines and C. A. A. Bloomquist, 173–184. **X-ray fluorescence analysis of plutonium,** W. S. Turnley, 189–195. **Quantitative gamma-ray spectrometric analysis of nuclide mixtures. Consecutive standard sources nullification,** D. G. Olson, 201–208. **Spectrochemical analysis of "fissium" for cerium and lanthanum,** G. W. Boyes, jun., J. B. Ramsay and R. T. Phelps, 209–214. **Quantitative determination of several short-lived iodine, barium and strontium fission products in gas-cooled reactor effluents,** L. L. Reed, M. N. Myers and W. W. Sabol, 215–229. **Radiochemical technique for determining fissionable material contamination on completed reactor fuel assemblies,** D. G. Miller and M. B. Leboeuf, 230–236. **Spectrophotometric determination of alloying and fission products elements in non-irradiated plutonium "fissium" alloys,** G. R. Waterbury and C. F. Metz, 237–245. **Fission-product analysis of fast-reactor plutonium fuels,** J. W. T. Meadows, G. M. Matlack and G. B. Nelson, 246–253. **Concentration of radioactivity and detection of cobalt-60 and zinc-65 in rain-out,** H. L. Krieger, J. E. Gilchrist and S. Gold, 254–264. **Determination of zirconium-95 plus niobium-95 by anion-exchange separation from other fission products,** A. C. Leaf, 265–272. **Separation and radioactive assay of fission products from samples obtained from high-temperature pressurised-water loops,** C. J. L. Lock and L. C. Bogar, 273 (summary only). **Determination of the distribution of fission xenon in irradiated uranium dioxide fuel elements,** W. W. Morgan, R. G. Hart, F. C. Miller and W. J. Olmstead, 275.

2271. **o-Hydroxybenzenesulphinic acid as an analytical reagent.** I. P. Alimarin and D. I. Kuznetsov. *Doklad. Akad. Nauk SSSR*, 1960, **131** (4), 821–824; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 76,961.—o-Hydroxybenzenesulphinic acid has been synthesised and its complexes with various metals have been studied. K. R. Cook

2272. **Rapid purification of tetrabutylammonium iodide for polarography.** J. Paściak (Chemical Works, Oświęcim, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 657–661.—*Procedure*—Dissolve 5 g of tetrabutylammonium iodide in 50 ml of boiling benzene, add 5 ml of dimethylformamide and cool rapidly. Filter off the crystals, wash with 5 ml of benzene - dimethylformamide (9:1), and dry *in vacuo* (<5 torr) for 2 hr. The product is as polarographically pure as that obtained by crystallisation from methanol - acetone, and can be used in dimethylformamide media but not in ethanolic media. P. Brych

2273. **Applications of the metal pyridine thiocyanate reaction to qualitative analysis.** G. H. Ayres and S. S. Baird (Univ. of Texas, Austin, U.S.A.). *Anal. Chim. Acta*, 1960, **23** (5), 446–448 (in English).—*Test for cations*—To a few drops of the sample soln. add 1 drop of a soln. containing 8% of pyridine and 3% of KSCN, and extract with 1 or 2 drops of $CHCl_3$. The following metals yield distinctive colours in the extract, and the sensitivities are indicated in p.p.m.—Cu, green, 0·1; Ni, sky blue, 2; Co, pink - red, 1; Fe^{II}, lemon yellow, 0·1; Mn^{II}, pale pink, 10. *Test for anions*—To 0·1M-$CuSO_4$ add pyridine until no further darkening occurs. Add 1 or 2 drops of this soln. to a few drops of the sample soln. and extract with 1 or 2 drops of $CHCl_3$. The following anions yield the colours stated—SCN^-, emerald green; OCN^-, yellow - green; CN^-, greenish yellow; peroxydisulphate, yellow - green; I^-, brown; Br^-, blue - green. *Test for aliphatic tertiary amines and pyridine bases*—These substances yield a green ppt. with 0·1M-$CuSO_4$ that has been decolorised with 10% KSCN soln. H. N. S.

2274. **Derivatives of biacridyl as indicators in the titration of weak acids.** M. Turowska (Dept. of Inorg. Chem., Univ., Łódź, Poland). *Chem. Anal., Warsaw*, 1960, **5** (5), 815–821.—The value of allyl, phenyl, propyl and tolylderivatives of biacridyl as chemiluminescent indicators for the titration of 0·1N or 0·01N soln. of acetic, n-butyric, citric, formic, propionic and tartaric acids is established, especially for coloured soln. The titration is carried out in the dark, in the presence of 3% H_2O_2 soln. (5 ml per 25 ml of soln.). The accuracy is ± 0·1%. The method is applied to the analysis of beer. B. K.

2275. **2,3-Dihydroxy-1-(2-pyridylazo)naphthalene-6-sulphonic acid and 4-(2-pyridylazo)orcinol, two new chelatometric indicators.** M. Hniličková and L. Sommer (Inst. Anal. Chem., Univ., Brno, Czechoslovakia). *Z. anal. Chem.*, 1960, **177** (6), 425–429 (in German).—The synthesis of 2,3-dihydroxy-1-(2-pyridylazo)naphthalene-6-sulphonic acid (**I**) and of 4-(2-pyridylazo)orcinol (**II**) is described and the sensitivity of the compounds towards metal ions compared with that of other indicators. The determination of Zn, Cd or Pb at pH 8 to 9, with **I**, and that of Cu at pH 3·3 is described; Cu is also determined at pH 2·7 in the presence of **II**, the relative error being < 1%. P. D. Parr-Richard

2276. **Synthesis of new phthalein indicators for complexometric titrations.** M. Wroński (Univ., Łódź, Poland). *Chem. Anal., Warsaw*, 1959, **4** (3), 641–642.—Synthesis and properties of oxine blue (**I**), hydrobenzamide blue (**II**) and catechól blue (**III**) are described. **I** is prepared from 8-hydroxyquinoline and *o*-(*p*-hydroxybenzoyl)benzoic acid and is suitable for determining alkaline-earth metals with EDTA. Methods of preparation of **II** and **III** are also given. Their properties are similar to those of **I**. N. E.

2277. **Chlorite as an oxidising agent in titrimetric analysis.** J. Minczewski and U. Glabisz (Dept. of Anal. Chem., Tech. Univ., Warsaw, Poland). *Talanta*, 1960, **5** (3–4), 179–188 (in English).—Sodium chlorite soln. (0·1N) is stable for at least 3 months if stored in the dark. With a platinum - S.C.E. system it can be used for the potentiometric titration of the following reducing substances. (*a*) Sulphite gives recoveries of 94% of the theoretical in the pH range 4·0 to 4·6; quant. results can be obtained by standardising against Na_2SO_3. (*b*) Iodide in N-H_2SO_4 soln. can be titrated with an accuracy of $\simeq$ 0·2%. (*c*) Bivalent Fe is titrated quant. in 2N-HCl - 2N-H_2SO_4 soln., with added iodide as catalyst; Sn^{II} gives a separate potential rise and can be used to reduce Fe^{III}. (*d*) Arsenite can be titrated in 5·5N- or 2N-HCl soln., with iodate as catalyst, with an accuracy of $\simeq$ 0·5%. W. T. CARTER

2278. **Complexometric analysis. IV. Anion analysis and physical methods.** J. A. R. Genge (Battersea Coll. Technol., London, England). *Lab. Practice*, 1960, **9** (11), 790–792.—The use of complexometric methods for the determination of anions and the applications of physical methods for end-point detection are reviewed. N. E.

2279. **Trace analysis.** Summer Symposium of the Analytical Division, American Chemical Society, Houston, Tex., 1960. *Anal. Chem.*, 1960, **32** (12), 1595–1598.—A summary of the proceedings, by W. W. Brandt, is published.

2280. **Ammonium hydrogen sulphate fusion. Applications to trace analysis by spectrochemical and other techniques.** C. Feldman (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1727–1728.—The advantages of NH_4HSO_4 over $K_2S_2O_7$ as a fusion agent for such materials as corrosion scales, refractory oxides or insoluble fluorides are discussed. Alloys of Nb and rare-earth metals have been dissolved in this reagent without the use of HF. Applications to plutonium analysis and the analysis of UF_4 are included. E. G. CUMMINS

2281. **Standard barium sulphate suspensions [for turbidimetry].** J. F. Boyd and J. W. Sommerville (Res. Dept., Roy. Maternity and Women's Hospital, Rottenrow, Glasgow, Scotland). *J. Clin. Path.*, 1960, **13** (1), 85–86.—It is shown that the temp., the order of mixing of the reagents, and the state of the volumetric flask all affect the extinction of barium sulphate suspensions used as standards in turbidimetry. The rate of mixing has little effect. The following reproducible procedure is recommended. The acid (0·2N-H_2SO_4) (50 ml) is placed in a dry 100-ml volumetric flask in a water bath at 37°. When the acid has attained the temp. of the bath, 1·15% $BaCl_2.2H_2O$ soln. (3 ml) is added, with gentle agitation, and after 10 to 15 sec. the flask is removed from the bath and cooled in running water whilst continuing the agitation. The vol. is then made up to 100 ml with 0·2N-H_2SO_4 and the flask is inverted several times. The extinction of this suspension is equivalent to 10 Maclagan units or 20 Kunkel units. R. A. BRENAN

2282. **Repeated extractions: a method of analysing a mixture of labelled compounds.** G. Rudstam (CERN, European Org. for Nucl. Res., Geneva, Switzerland). *Anal. Chem.*, 1960, **32** (12), 1664–1666.—Simple apparatus is described for extracting compounds with different partition coeff. in the same solvent. The compounds can be labelled with the same tracer atom. The soln. is extracted repeatedly ($\simeq$ 6 times) with fresh solvent and the activity of each portion is measured. A fixed schedule is kept for the procedure to allow corrections to be made for interchange between the components. Conditions necessary for independent and dependent constituents are developed. The partition coeff. must differ by a factor > 2, and should not depend on the concn. of the solutes. The rate constants should be between 0·01 and 0·2 per min. Applications suggested are the analysis of nitrosylruthenium complexes and the determination of ferrous - ferric ratios. H. A. FONER

2283. **Applications of zone melting to analytical chemistry.** W. G. Pfann and H. C. Theuerer (Bell Telephone Lab., Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1574–1578.—Analytical aspects of zone melting, and controlled freezing in general, arising from advances in the semi-conductor field, are reviewed. Micro-techniques, the concentration of impurities, direct analysis and the provision of high-purity standards are included in the discussion and bibliography. (39 references.) E. G. CUMMINS

See also Abstracts—**2299**, Advantages of acetate buffer in complexometry. **2504**, Phenitrazole as diazo coupling agent.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

2284. **Detection of very small amounts of inorganic gases with an ionisation detector.** R. Lesser (Vakuummetallurg. Lab. W. C. Heraeus G.m.b.H., Hanau, Germany). *Angew. Chem.*, 1960, **72** (21), 775–777.—If the carrier gas (Ar) entering a β-ray ionisation detector contains a small but constant amount of an organic vapour, H, N, O and CO, after separation by chromatography, can be detected with high sensitivity (10^{-5} ml) by measuring the reduction they produce in the ionisation current. Small amounts of gas liberated from metals (*e.g.*, Zircaloy-2, niobium) by vacuum fusion are passed through a column of molecular sieve (5 A) (120 cm × 0·4 cm) at 22°. A solid organic compound (*e.g.*, 1,2,4,5-tetrachlorobenzene) is placed in a glass tube between the column and the detector. The detector is operated at 1750 V. J. W. PRICE

2285. **Fractional extraction of cations and anions.** E. Jackwerth and H. Specker (Inst. f. Spektrochem. und angew. Spektroskopie, Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 1960, **177** (5), 327–333 (in German).—It is shown that, by the addition of KI soln. to a dil. HNO_3 soln. of Hg^{2+}, Bi^{3+}, Cd^{2+}, In^{3+} and Zn^{2+}, these elements can be successively extracted with tributyl phosphate or cyclohexanone in the order given. Similarly anions (I^-, Br^- and Cl^-) can be extracted with HgI_2 in tributyl phosphate. The determination of these cations in the aq. phase by X-ray fluorescence spectrometry and of anions by conductimetric extraction - titration is discussed. B. B. BAUMINGER

2286. **Precipitation chromatography: diffusion and precipitation of metal sulphides on agar-gel columns.** J. D. Spain (College of Mining and Technol., Houghton, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1622–1624.—Columns (12 cm × 6 mm) of purified agar gel impregnated with 2M-Na acetate buffer and 0·1M-ammonium sulphide are used to produce characteristic bands of sulphides. The soln. of metal ions (≃ 5 mg of metal per ml) in 6M-HCl is added to the column to a depth of 0·5 cm and observations are made after 24 and 48 hr. The bands of single metal sulphides, characteristic bands of the sulphides of 2 or more metals, and the appearance of the liquid above the column all contribute to a system of qualitative analysis. Sulphide bands are obtained for Sn (yellow), Hg (black), Cu (greenish black over brown), Pb (blue-grey), Bi (white BiOCl; brown Bi_2S_3), Cd (opaque yellow), Sb (orange), As (clear yellow), Zn (multiple white bands), Co (multiple smoky-grey bands), Ni (smoky grey), and Fe (black). The accuracy varied from 66 to 100 correct identifications in 100 analyses. The relative spacing of the bands is constant.

H. A. FONER

2287. **Utilisation of the (α, *n*) reaction for quantitative determination of beryllium, boron and fluorine in ores and their enrichment products.** I. N. Plaksin, V. N. Smirnov and L. P. Starchik. *Atomnaya Energiya*, 1960, **9** (5), 361–363.—The following nuclear disintegration reactions—

(*i*) $^{9}Be + {}^{4}He \rightarrow {}^{12}C + {}^{1}n$

(reaction yield, 80 neutrons per 10^6 α-particles),

(*ii*) $^{19}F + {}^{4}He \rightarrow {}^{22}Na + {}^{1}n$

(reaction yield, 12 neutrons per 10^6 α-particles),

(*iii*) $^{10}B + {}^{4}He \rightarrow {}^{13}N + {}^{1}n$, and

(*iv*) $^{11}B + {}^{4}He \rightarrow {}^{14}N + {}^{1}n$

(reaction yield, 24 neutrons per 10^6 α-particles),

have been used for the rapid quant. determination of Be, B and F in ores and products obtained during their enrichment. The number of neutrons emitted during bombardment of such products with α-particles is proportional to the concn. of Be, B and F therein, since the other elements present (Al, Si, C and O) give considerably smaller neutron yields (0·74, 0·16, 0·11 and 0·07 for 10^6 α-particles, respectively). The apparatus and procedure are fully described; ^{210}Po serves as a source of α-particles (activity 250 mC). The method is rapid, simple and safe, and has an accuracy of 1·5 to 2%. It can be applied to the determination of Be and B in alloys, and is also applicable to the field assay of Be- and B-containing ores.

W. ROUBO

2288. **Chromatographic separation of inorganic ions on glass-fibre strips using fused salts as eluent.** G. Alberti and G. Grassini (Ist. Chim. Gen. ed Inorg., Lab. Chim. della Div. Geomineraria del C.N.R.N., Rome). *J. Chromatography*, 1960, **4** (5), 425–426 (in English).—A number of metal ions have been separated on glass-fibre paper by ascending chromatography at 160° with $LiNO_3$-KNO_3 eutectic, with and without added KCl, as eluent.

G. BURGER

2289. **Determination of lead, cadmium and zinc ions in [the presence of a] large excess of indium ions by alternating-current polarography.** Takeo Takahashi and Hideko Shirai (Inst. Ind. Sci., Univ. Tokyo, Japan). *Talanta*, 1960, **5** (3–4), 193–198 (in English).—The a.c. polarogram of Pb, Cd, Zn and In in M-H_3PO_4 shows clearly defined peaks for Pb, Cd and Zn at − 0·78, − 0·93 and − 1·33 V *vs.* the mercury pool. A linear relationship between peak height and metal-ion concn. is obtained in the range 0·05 to 0·25mM. Indium is without effect up to 0·07M, but above this level the hydrogen discharge wave begins to obscure the peak for Zn. Thallium interferes by forming a wave between Pb and Cd, and halide ions interfere by forming a reducible complex with In, which also forms a wave between Pb and Cd.

W. T. CARTER

2290. **X-ray spectrographic determination of zirconium, tungsten, vanadium, iron, titanium, tantalum and niobium oxides: application of the correction factor method.** B. J. Mitchell (Technol. Dept., Union Carbide Metals Co., Niagara Falls, N.Y.). *Anal. Chem.*, 1960, **32** (12), 1652–1656.—The combined oxides are prepared by pptn. from soln. and ignition, and the finely ground product (≃ 0·5 g) is compressed into a briquette (0·875 to 1·25 in. diam.) at 10,000 to 20,000 lb pressure. Oxide standards for Nb, Ta, W and Zr are prepared by mixing the pure oxides, but those for Fe, Ti and V should be prepared by pptn. and ignition. Calibration is simplified by arithmetic correction factors for inter-element effects. Simultaneous measurements of all 7 elements (concn. 0·1 to 99·9%) can be made in < 2 min. An X-ray analysis takes < 15 min. The instrumental precision is better than ± 0·5% for high percentages of components. It is confirmed that longer counting times improve precision. The instrument used is an X-ray industrial Quantometer.

H. A. FONER

2291. **Method for detecting hydrogen in gas mixtures.** J. R. Young and N. R. Whetten (General Electric Res. Lab., Schenectady, N.Y., U.S.A.). *Rev. Sci. Instrum.*, 1960, **31** (10), 1112–1114.—The sample gas is passed over an evacuated palladium thimble at 500°. The ultimate pressure of H accumulating in the interior of the thimble is measured with a thermocouple gauge or a mercury manometer. By this method it is possible to detect H at a partial pressure of 10^{-7} torr.

G. SKIRROW

2292. **Neon as eluent in the gas-chromatographic determination of helium in gases.** E. Zieliński (School of Mining and Metallurgy, Kraków, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 605–610.—The introduction of neon as eluent in the columns previously described (*cf. Anal. Abstr.*, 1961, **8**, 19) provided a rapid and accurate method for determining He in neon (10 to 15 min.) and natural gas (30 to 40 min.). Slight modifications of the apparatus were made in order to reduce the sample volume.

P. BRYCH

2293. **Chromatographic separation of alkali-metal ions on paper impregnated with ammonium molybdophosphate.** G. Alberti and G. Grassini (Ist. Chim. Gen. ed Inorg., Lab. Chim. Div. Geomineraria del C.N.R.N., Rome). *J. Chromatography*, 1960, **4** (5), 423–425 (in English).—Procedures are described for preparing the paper and separating the alkali metals from a mixture containing all of them. The metals are separated into groups with one solvent, the chromatogram is cut into sections, and these are re-developed with other solvents. The solvents used are mixtures of HNO_3 and NH_4NO_3 in different concn.; 95% ethanol is used to separate Li and Na.

G. BURGER

2294. **Circular paper-chromatographic method for analysis of certain alkali- and alkaline-earth-metal ions.** M. L. Bhatnagar, N. K. Mathur and Dalchand (Chem. Dept., Jaswant College, Jodhpur). *J. Sci. Ind. Res., India, B*, 1960, **19** (12), 501.—The separation and determination of Na^+, K^+, Ca^{2+} and Mg^{2+} by circular paper chromatography, with ethanol - 2N-butyric acid (5:1) as solvent, is described. Quantitative determinations can be made by elution of the appropriate bands with suitable solvents (dil. HCl for Ca^{2+} and Mg^{2+} and anhyd. dimethylformamide for Na^+ and K^+); Ca^{2+} and Mg^{2+} are determined with EDTA, and Na^+ and K^+ are determined colorimetrically at 605 mμ with violuric acid. An accuracy of $\pm$ 2% is claimed in most cases. I. A. SIMPSON

2295. **Determination of sodium by atomic absorption spectroscopy.** J. W. Robinson (Esso Research Lab., Baton Rouge, La., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (5), 458–461 (in English).—The effect of flame emission is eliminated by modulating the hollow-cathode sodium lamp with a light chopper and tuning the detector to the same frequency. Interference from even large amounts of K and Li is thus avoided. H. N. S.

2296. **Flame-photometric determination of sodium in alkaline-earth carbonates.** J. M. Hibbs and G. W. McDonald (A.E.I. Res. Lab., Harlow, Essex, England). *Analyst*, 1960, **85**, 846–847.—The sample ($\geq$ 0·25 g containing $\geq$ 200 μg of Na) is dissolved in the minimum of 5N-HNO_3 and the soln. is diluted to 5 ml. To this soln. at 60° is added 10% aq. ammonium carbonate soln. (2·5 ml) and the cooled liquid is set aside for 5 min. The ppt. is separated and washed by centrifuging, and the combined supernatant liquid and washings are boiled to expel CO_2, diluted to 25 ml and sprayed into an EEL flame photometer, previously set to full-scale deflection with a standard soln. containing 10 p.p.m. of Na and the same concn. of reagents as the test soln., and to zero with a soln. containing the reagents only. The deflection is referred to a calibration graph. A. O. JONES

2297. **Determination of potassium by means of its natural radioactivity.** N. I. Pavlova and T. M. Khrenkova. *Zavod. Lab.*, 1960, **26** (11), 1201–1202.—With the apparatus described, determinations accurate to within $\pm$ 1% can be obtained in 2 min. with contents of K of $\simeq$ 50%, in 10 min. with contents of $\simeq$ 10%, and in 3 hr. with contents of $\simeq$ 0·05%. G. S. SMITH

2298. **Volumetric determination of trace amounts of copper with oxine blue.** M. Wroński (Dept. Chem. Technol., Univ., Łódź, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 597–599.—Oxine blue (*cf. Anal. Abstr.*, 1961, **8**, 2276) is intensely coloured in alkaline soln. and is decolorised by Cu^{2+}, as the pink colour of the oxine blue - Cu^{2+} complex is discharged in dilute soln. The reaction is more sensitive than that with diethyldithiocarbamate and is fairly specific. Zinc, Cd, Pb, Co and Mg form complexes which do not interfere up to a 100-fold excess; corrections can be applied for still larger amounts. Interference from Hg^{2+} is eliminated with KI. *Procedure*—To the sample (containing 1 to 20 μg of Cu^{2+}) add 5 ml of 0·1N-aq. NH_3, dilute to 50 ml and titrate with standard oxine blue soln. in 8% ethanol until the colour matches that of a blank prepared by titrating 50 ml of 0·1N-aq. NH_3 with oxine blue to a definite blue colour. P. BRYCH

2299. **The basic problems of complexometry. III. Some advantages of acetate buffer.** W. Berndt and J. Šára (Spolana n.p., Neratovice, Czechoslovakia). *Talanta*, 1960, **5** (3–4), 281–283 (in English).—Copper can be titrated directly with EDTA at pH 5 to 6 with xylenol orange or methylthymol blue as indicator if acetate buffer is substituted for hexamine buffer. The titration is normally carried out at 70°, but can be made at room temperature if small amounts of substances capable of forming substitution-labile copper complexes, notably 1,10-phenanthroline and 2,2′-bipyridyl, are present. W. T. CARTER

2300. **Preliminary study of the photometric determination of copper with ammonia and phenol.** N. M. Paunović (Inst. Chem., Med. Fac., Univ., Belgrade). *Bull. Sci., Yougoslavie*, 1960, **5** (4), 101–102 (in German).—The conditions (*e.g.*, temp. and time of reaction) governing the use of this reaction for the quant. determination of Cu^{2+} have been studied. The reaction is carried out in 3M-aq. NH_3 (50 ml) with the addition of phenol (0·5 g). A substance isolated from such a mixture consisted of a mixture of $[Cu(NH_3)_4]SO_4$ and $[Cu(C_6H_5OH)_4]$-SO_4. For analytical use, extinctions are measured at 620 mμ. At room temp., the reaction is incomplete after 80 min. but, if the reaction mixture is heated for 2 hr. at 50° and then cooled, the colour is relatively stable. Under these conditions Beer's law is valid over the range 10 to 20 p.p.m. of Cu ($E^{1\%}_{1\,cm}$ = $\simeq$ 250). G. RUSSELL

2301. **Application of metallochromic indicators in colorimetry. I. The spectrophotometric determination of minute amounts of copper with analogues of glycine thymol blue.** M. Koch, V. Svoboda and J. Körbl (Dept. of Chem., Sch. Agric., Brno, Czechoslovakia). *Talanta*, 1960, **5** (3–4), 141–146 (in English).—Proline thymol blue is recommended as the best of five similar compounds for the spectrophotometric determination of Cu. It has a high sensitivity (pD = 7·6), and the complex with Cu is unaffected by pH over the range 4·9 to 5·4, and obeys Beer's law up to 25 μg of Cu in 25 ml of soln. The complex forms rapidly at room temperature and the colour does not fade for several days. Cobalt, Zn, Ni, Pb, U, Be and Fe^{II} interfere, but interference due to Fe^{II} can be avoided by oxidation to Fe^{III} and masking with NH_4F. Iodide, dithionite, ferro- and ferri-cyanide, oxalate, citrate, tartrate and all anions that form complexes with Cu interfere. W. T. CARTER

2302. **Determination of copper by means of atomic absorption spectroscopy.** A. Strasheim, F. W. E. Strelow and L. R. P. Butler (Nat. Phys. and Chem. Lab., S. African Council for Sci. Ind. Res., Pretoria). *J. S. Afr. Chem. Inst.*, 1960, **13** (2), 73–81.—The copper content of copper ores (0·2 to 25% of Cu) has been determined by atomic absorption techniques with a coeff. of variation of $\pm$ 6·2%. The ore (0·5 g) is digested with HF and HNO_3 for 40 min., diluted to 200 ml, filtered and, if necessary, further diluted to a Cu concn. of $\geq$ 100 p.p.m.; Ca, Na, Fe, K, Al, Co, SO_4^{2-} and Cl^- do not interfere. A Hilger atomic absorption attachment was used with a Uvispek or Zeiss spectrophotometer, with the burner modified to burn "Handigas"; the current of the hollow cathode lamp had to be 40 mA because of the limited sensitivity of the detector system; the resonance line at 3247 A was used with a slit-width of 0·2 mm and a rate of sample consumption of 20 ml per min. T. R. ANDREW

2303. **Spectrographic determination of impurities in silicon - copper alloy and in trichlorosilane.** K. K. Popokov, S. L. Lel'chuk and A. S. Kudryatseva. *Plast. Massy*, 1960, (1), 39–41; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 77,118.—Iron, Mg, Al, Bi, Sn, Ti, Ca, Pb and Sb were determined in a Si - Cu alloy (10 to 20% of Cu) used for the production of organosilicon compounds. Place the alloy (0·1 g) in a graphite cup (internal diam. 4 mm, depth 8 mm) attached to a holder with a platinum wire. Slowly heat to 800° and then connect up to an 8-amp. a.c. arc with an upper hemispherical graphite electrode. Photograph the spectra and compare with standards prepared by saturating CuO and Si with a metal salt soln. Determine the concn. in the ranges 0·0005 to 0·1 and 0·01 to 2%, according to the element. To determine very low concn. of Fe, Al, Cu, Pb or Mg in the hydrolysis product of trichlorosilane, evaporate the sample (0·05 g) in the graphite cup. K. R. Cook

2304. **The analysis of beryllium and beryllium oxide. IV. Determination of cobalt.** J. O. Hibbits, A. F. Rosenberg and R. T. Williams (Aircraft Nuclear Propulsion Dept., General Electric Co., Cincinnati, Ohio, U.S.A.). *Talanta*, 1960, **5** (3–4), 250–253 (in English).—The method is a modification of that of Brown and Steinbach (*Anal. Abstr.*, 1960, **7**, 2737). Beryllium and other elements are removed by extraction with acetylacetone at pH 4·0, NaSCN is added, Co is extracted as the thiocyanate complex with more acetylacetone and determined by measuring the extinction at 625 mμ. The complex is stable for at least 2 weeks and Beer's law is obeyed up to 8 μg of Co per ml. Of the 68 elements investigated, only Cr and Mn interfere in 10-mg amounts and must be removed by adsorption on anion-exchange resin. Recoveries of 98 to 102% were obtained on synthetic samples containing 100 μg of Co. W. T. Carter

2305. **Determination of oxygen in beryllium metal by the inert-gas fusion method.** S. Kallmann and F. Collier (Res. Div., Ledoux and Co., Teaneck, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1616–1619.—A modified Leco oxygen analyser is used. The sample is heated (2600°) in a graphite crucible by an induction furnace, with purified Ar as the carrier gas. The CO formed is oxidised by I_2O_5 to CO_2, which is absorbed in $Ba(OH)_2$ soln. and measured conductimetrically. A special graphite crucible (2·25 in. long × 0·875 in. in diam., with a central hole 0·625 in. in diam.) is used, mainly to prevent carbon black (insulation) from being blown back. The best results are obtained with a nickel flux. The crucible is out-gassed at 2700° for 10 min., and the apparatus blank is obtained for a 7-min. cycle (1·5 min. at 2600° and a 5·5-min. flushing with Ar). A flux blank (on 0·4 g of copper foil and 1 g of nickel sheet) is obtained in the same way, and should be ⩾ 0·5 ohm. Standard curves are obtained with PbO or Ag_2O (≡ 100 to 400 mg of O) wrapped in copper foil (100 mg). The graph of corrected readings *vs.* O content is linear up to 400 μg. The sample (0·25 to 0·1 g, according to the O content) is wrapped in copper foil and placed in the apparatus with ten times its own wt. of nickel. The determination is carried out as described above. The method gives good results on standard samples. H. A. Foner

2306. **Rapid determination of water of hydration in magnesium perchlorate desiccant.** G. F. Smith (Noyes Chem. Lab., Univ. Illinois, Urbana, U.S.A.). *Talanta*, 1960, **5** (3–4), 189–192 (in English).—The sample (20 g), wrapped in filter-paper, is dropped into water (75 ml) in a 300-ml Dewar flask. The flask is swirled to ensure dissolution of the sample, and the equilibrium temperature rise is measured after 20 to 25 sec. The H_2O content of the sample is read off from a graph previously prepared from samples of known H_2O content. The temperature rise varies linearly with H_2O content from 37·5° for the anhydrous salt to 17·6° for the dihydrate (13·9% of H_2O). The sample is wrapped in filter-paper to prevent the loss of heat as steam, particularly from samples containing < 5% of H_2O. W. T. Carter

2307. **The separation of calcium from magnesium.** I. Sarudi (v. Stetina) (Chem. Untersuchungsamt, Szeged, Hungary). *Z. anal. Chem.*, 1960, **177** (6), 404–407 (in German).—Pptn. of Ca oxalate at room temp. by the method described gives a dense, easily collected ppt. Large amounts of H_3PO_4 do not interfere. *Procedure*—To 150 ml of soln. containing 2N-acetic acid (10 ml), 2 to 3 g of NH_4Cl and ⩾ 0·1 g of Ca plus Mg, slowly add 2 to 3 drops of ammonium oxalate soln. (a 2-fold excess in 20 ml of H_2O), stirring rapidly. After 2 min., run in 10 ml of oxalate soln. (40 to 50 drops per min.) and the next 10 ml more rapidly. Continue stirring for 10 min. and allow to stand for 4 hr. Filter and wash the ppt., then ignite and weigh it as $CaCO_3$. P. D. Parr-Richard

2308. **New selective metallochromic reagent for the detection and chelatometric determination of calcium.** R. A. Close and T. S. West (Univ. of Birmingham, England). *Talanta*, 1960, **5** (3–4), 221–230 (in English).—The synthesis, structure and properties of cyclotris-7-(1-azo-8-hydroxy-naphthalene-3,6-disulphonic acid) (Calcichrome) are described. It gives colour reactions with only 8 cations in the pH range 2 to 13 and with Ca^{2+} alone at pH 13. As a spot reagent for Ca^{2+}, 0·25 μg can be detected at a dilution limit of 1 in 10^6 if the alkalinity is maintained between 0·02 and 0·04N. Interference from heavy metals can be reduced by the addition of acetone saturated with H_2S; Ba^{2+}, Mg^{2+}, Na^+, PO_4^{3-}, SO_4^{2-} and oxalate interfere, but the detection of Ca^{2+} is possible in the presence of an 8-fold excess of Ba^{2+}, Sr^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Mg^{2+}. The reagent can also be used as an indicator for the titration of Ca^{2+} in the presence of up to a 12-fold excess of Ba^{2+} with *trans*-1,2-diaminocyclohexanetetra-acetic acid at pH 13. The results are accurate to within 0·4%. Strontium is titrated with the Ca^{2+} and must be pptd. with $(NH_4)_2SO_4$, but under these conditions the accuracy is reduced. W. T. Carter

2309. **Colorimetric determination of calcium.** V. M. Dziomko, K. A. Dunaevskaya, K. A. Smirnova, K. E. Kalinina, L. K. Kuznetsova and V. I. Maslinikova. U.S.S.R. Pat. 128,196 (28th April, 1960).—The reagent used is 2-hydroxy-2'-(2-hydroxy-1-naphthylazo)-5-methylazoxybenzene (azo-azoxy B.N.) (**I**), which in alkaline medium reacts with Ca but not with Ba, Sr, Mg or Be; the soln. of **I** in CCl_4 changes from orange - pink to colourless in the presence of Ca. In the presence of Cu and Co the colour changes to purple and violet - brown, respectively. Other cations do not affect the colour. No interference in the determination of 5 μg of Ca in 5 ml is caused by 50 μg of Na, K, Rb, Cs, Ag, Mg, Zn, Sr, Ba, Hg, Be, Al, V, In, La, Ge, Pb, Hf, Y, Bi, Sn, Se, Mo, Tl,

W, Re or Ni; Cd, Sc, Ga, Ti, Zr, As, U, Mn, Fe, Co and Cu interfere. To determine Ca in the chlorides, nitrates or sulphates of K or Na, to 1 ml of soln. containing 0·1 g of salt in a separating-funnel add 3 ml of CO_2-free water, 1 ml of 20% NaOH soln., 5 ml of CCl_4 and 0·35 ml of a 0·04% soln. of **I** in CCl_4, shake for 2 min., separate the lower CCl_4 layer into a 10-mm cell and measure the extinction against CCl_4. Construct a calibration curve similarly from soln. containing 0 to 20 μg of Ca.

C. D. KOPKIN

2310. **Determination of sodium sulphate, calcium chloride and sodium chloride in gypsum plaster.** E. Hoffmann (C.S.I.R.O., Div. of Bldg Res., Highett, Victoria, Australia). *Z. anal. Chem.*, 1960, **177** (5), 353–356 (in English).—Procedures for these determinations are described. (*i*) For the determination of Na_2SO_4 in the presence of $CaSO_4$ and NaCl, Ba chloranilate (**I**) is added to the test soln.; chloranilic acid is liberated in an amount equiv. to the Na_2SO_4 only, and is measured colorimetrically. The $CaSO_4$ also reacts with **I**, but the Ca chloranilate formed is insoluble and does not affect the production of the colour. (*ii*) For the determination of $CaCl_2$ in the presence of $CaSO_4$ and NaCl, **I** is added to the test soln. to remove $CaSO_4$ as insol. Ca chloranilate, then chloranilic acid is added in excess, the mixture is filtered, and the unchanged acid is measured colorimetrically. (*iii*) For the determination of NaCl in the presence of $CaCl_2$ and $CaSO_4$, $CaSO_4$ is removed from the test-soln. after conversion into $BaSO_4$ by reaction with a small excess of $BaCl_2$; Ag chloranilate is then added and reacts with the unchanged $BaCl_2$ to form insol. **I**, and chloranilic acid equiv. to the NaCl is liberated and measured colorimetrically. Details of standardisations for the three procedures are given.

H. I. F.

2311. **Selective separation of radioactive strontium.** K. H. Lieser and W. Hild (Eduard-Zintl-Inst. für Anorg. u. Phys. Chem., Tech. Hochsch., Darmstadt, Germany). *Naturwissenschaften*, 1960, **47** (21), 494–495 (in German).—A packing for chromatographic columns incorporating $BaSO_4$ is prepared by treating silica gel (**I**) with $Ba(OH)_2$ soln., washing out any unbound $Ba(OH)_2$, and converting the barium silicate into $BaSO_4$ with H_2SO_4 (1:1). The $BaSO_4$ is tightly bound to the **I**, constitutes 30 to 40% of the total wt., and is available for cation exchange. This exchange is highly selective; Ba, Ra and Sr are preferentially exchanged (in that order), Ca much less readily. Mono- and ter-valent ions are not exchanged. The Sr^{2+} penetrate the packing by mixed-crystal formation, but Ca is bound at the surface. The technique is applied to the examination of tap-water, from which Sr is completely removed; Fe is also removed (as hydroxide) and occludes any ^{90}Y present.

J. P. STERN

2312. **Cation-exchange behaviour of barium on Dowex 50W-X8. Separation of mixtures.** Shripad M. Khopkar and Anil K. De (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1960, **23** (5), 441–445 (in English).—Soln. of HNO_3, HCl, NH_4Cl, $NaNO_3$, NaCl, ammonium acetate, citric acid, tartaric acid and EDTA were examined as eluents for Ba^{2+} on a Dowex 50W-X8 column. From the results obtained, methods were devised for the separation of Ba from U^{VI}, Cu^{II}, Hg^{II}, Cs, Zn, Cd, Ag, Ce^{IV}, Zr, Th, Fe^{II} and Bi^{III}.

H. N. S.

2313. **Determination of zinc in basalt and other rocks.** L. F. Rader, W. C. Swadley, H. H. Lipp and C. Huffman, jun. (U.S. Geol. Surv., Denver, Colo.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 477–480.—The soln. in 1·2M-HCl is passed through an anion-exchange resin (Cl^- form), Zn being adsorbed. The Zn is then eluted with 0·01M-HCl and pptd. with diethyldithiocarbamate at pH 8·5 and the ppt. is extracted with $CHCl_3$. Zinc is then separated from the $CHCl_3$ with 0·16M-HCl and determined spectrophotometrically at 620 mμ with 2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene at pH 9·0. This is a highly sensitive method, combining selected features of several published techniques, and is particularly designed to determine Zn in rocks containing 10 to 20% of Fe and many other elements in amounts that interfere with the determination of Zn by other methods. The standard deviation ranged from 0·005 to 0·0002% of Zn for various rocks.

R. A. HOWIE

2314. **Co-precipitation of zinc, cadmium and mercury with copper anthranilate.** I. M. Korenman and M. N. Barÿshnikova. *Trudÿ Khim. i Khim. Tekhnol.*, 1959, (2), 385–392; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 76,948.—The pptn. of Cu by anthranilic acid in the presence of Zn, Cd or Hg is studied by micro- and semi-micro methods and controlled radiometrically (with the isotopes ^{65}Zn, ^{115}Cd and ^{203}Hg). It is established that co-pptn. is dependent on the pH of the medium, the temp. and duration of settling of the ppt. and the presence of impurities. Co-pptn. is decreased by lowering the pH and is slightly affected by a number of other factors.

K. R. COOK

2315. **Volumetric determination of cadmium, alone or in the presence of aluminium and lead.** I. Grecu, V. Handelsmann and E. Curea (Lab. Inorg. Chem., Fac. of Pharm., Cluj, Romania). *Rev. Chim., Bucharest*, 1960, **11** (10), 587–588.—The method is based on the formation by Cd of an insol. complex $[Cd(C_{13}H_{17}ON_2)_2](SCN)_2$ with SCN^- in the presence of amidopyrine, and the titration of the excess of SCN^-. *Procedure*—The sample soln. is acidified with 1 or 2 drops of conc. acetic acid and treated first with 25 ml of 4% amidopyrine soln., then with an excess (50 to 60 ml) of 0·1N-NH_4SCN, and diluted to 100 ml. The ppt. is allowed to settle and the filtrate is titrated against 0·1N-$AgNO_3$, with $(NH_4)_2SO_4.Fe_2(SO_4)_3$ as indicator. Aluminium, if present, is first removed by treatment with an excess of 4% amidopyrine soln. (about 35 to 40 ml), and proceeding as described above. Lead is removed initially by pptn. with 20% Na_2SO_4. Twelve results on amounts of Cd between 0·018 and 0·1 g gave a coeff. of variation of 0·17%.

H. SHER

2316. **Precipitation of mercury as phenazone bromomercurate(II) in the presence of iron.** I. M. Korenman and A. A. Tumanov. *Trudÿ Khim. i Khim. Tekhnol.*, 1959, (2), 406–409; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 77,032.—The pptn. is studied by a micro-method, the amount of pptd. Fe being determined radiometrically (with ^{59}Fe). The pptn. of a soln. 0·1N with respect to HNO_3 is carried out with a reagent (1 ml) consisting of phenazone (10 g) and KBr (20 g) in H_2O (70 ml). It is established that the co-pptn. of Fe^{3+} is dependent on the concn. of Hg, the amount of Fe present, the acidity of the soln., the temp. and duration of settling of the ppt. and the presence of impurities.

Although the amount of co-pptd. Fe is small, a quant. determination of Hg as $(C_{11}H_{12}ON_2)_2$.$H_2[HgBr_4].2C_{11}H_{12}ON_2$ is practically impossible.
K. R. Cook

2317. **Volumetric determination of mercurous ions with potassium ferrocyanide in the presence of diphenylcarbazone.** H. Basińska and A. Bukowska (Copernicus Univ., Toruń, Poland). *Chem. Anal., Warsaw*, 1960, **5** (5), 707–710.—A sample of $Hg_2(NO_3)_2$ dissolved in H_2O and acidified with HNO_3 is titrated with standard $K_4Fe(CN)_6$ soln. in the presence of the indicator (0·3% ethanolic diphenylcarbazone). At the end-point the violet - blue colour of the soln. is discharged. The best results (error $< 1\%$) are given when the concn. of sample is from 0·01M to 0·025M. B. K.

2318. **Back-titration with mercuric nitrate in alkaline medium. Analysis of ternary mixtures of mercury(II) with some other metals.** H. Khalifa and Farouk A. Osman (Microanal. Dept., Nat. Res. Centre, Dokki, Egypt). *Z. anal. Chem.*, 1960, **178** (2), 116–123 (in English).—Ternary mixtures containing Hg^{II} were analysed by a combination of methods. *Procedure for Hg, Cu and Th*—Determine the total metal content by back-titrating excess of EDTA (disodium salt) with $Hg(NO_3)_2$ at pH 9 to 10. Titrate Th in another aliquot at pH 1·7 with EDTA, with catechol violet as indicator. Determine Cu in a further aliquot with iodine - $Na_2S_2O_3$. *Hg, Zn and Mn*—Determine the total metals as described above. Titrate Hg potentiometrically with KI soln., with a silver amalgam indicator electrode. Then titrate Mn with EDTA at pH 10 in the presence of KCN and ascorbic acid, with Eriochrome black T as indicator. *Hg, Zn and Th*—Determine the total metals, Hg and Th as described above. Analyses of mixtures of Hg, Pb and Cu were unsuccessful.
P. D. Parr-Richard

2319. **Water-soluble boron in sample containers.** C. Huffman, jun. (U.S. Geol. Survey, Denver, Colo.). *U.S. Geol., Surv., Profess. Paper*, No. 400-B, 1960, 493–494.—Erratic spectrographic values for boron in rock samples were traced to boron contamination from paper pill-box containers. Water-soluble boron was extracted from the cardboard by heating in water on a steam bath for 3 hr. The volume was then adjusted to 100 ml per 2 g of cardboard, and boron was determined spectrophotometrically by the carminic acid method. All extractions were carried out in boron-free polyethylene beakers.
R. A. Howie

2320. **Fluorimetric determination of boron. Application to silicon, sea water and steel.** C. A. Parker and W. J. Barnes (Admiralty Materials Lab., Holton Heath, Poole, Dorset, England). *Analyst*, 1960, **85**, 828–838.—The ground silicon sample is cleaned with HCl and washed free from Cl^-. Boron is separated by heating the sample with dil. NaOH soln. at 350° and a pressure of 350 atm. when the Si is converted into SiO_3 and the B remains in soln. as BO_3^{3-}. An aliquot of the filtrate is distilled in a high vacuum and the BO_3^{3-} in the distillate are determined fluorimetrically after reaction with benzoin in an inert atmosphere in the presence of Na_2CO_3 and ethanol. For determination of B in sea water, 10 ml and then 60 ml of the diluted sample (1:9) are passed through a cation-exchange column (Amberlite IR-120, H^+ form), all but the last 30 ml being discarded. A 5-ml portion is treated with its equiv. of NaOH soln. and the BO_3^{3-} are determined fluorimetrically. Steel samples are dissolved in 5N-H_2SO_4. H_2O_2 is added to oxidise Fe^{2+}, the excess is removed by boiling and an aliquot of the filtered liquid (containing also the residue from the combustion in O of the filter-paper) is submitted to the high-vacuum distillation and fluorimetric procedure. In silicon the limit of detection is $\simeq 0{\cdot}03$ p.p.m., in sea water the precision is better than $\pm 2\%$, and in steel the limit of detection is $\simeq 1$ p.p.m.
A. O. Jones

2321. **Determination of boron in aluminium and silicon - aluminium alloys.** E. G. Towndrow and H. W. Webb (Johnson, Matthey & Co. Ltd., Exhibition Grounds, Wembley, Middx., England). *Analyst*, 1960, **85**, 850–851.—The sample (0·1 g) of filings or sawings in a nickel crucible is first sintered with Na_2O_2 and then fused. The melt is leached with water in a polyethylene beaker and the liquid is diluted to 250 ml in an acrylic resin cylinder and returned to the beaker. After the $Ni(OH)_2$ has settled, a 10-ml aliquot of the soln. is transferred by a Perspex pipette to a polyethylene or platinum vessel, its pH is adjusted to $\simeq 2$ with 2N-H_2SO_4 and it is then applied to a column of cation-exchange resin (Zeo-Karb 225, H^+ form) which is eluted with water (250 ml). The pH of the eluate is adjusted to 8 to 9 with Na_2CO_3 soln., the liquid is evaporated to dryness in a platinum dish, the residue is dissolved in 7·5 ml of water, and 7·5 ml of H_2SO_4 (4:1) is added. The soln. and washings of the dish with the H_2SO_4 are diluted to 20 ml, so that the acid content should now be 1:1. A 5-ml aliquot is treated with 5 ml of dianthrimide reagent (prep. described), then diluted to 50 ml with conc. H_2SO_4 and heated in a silica boiling-tube at 95° ± 1° for 16 hr. The extinction of the cold liquid is measured at 640 mμ and referred to a calibration graph. If the alloy is free from interfering elements (*e.g.*, Cr and V), the ion-exchange procedure may be omitted.
A. O. Jones

2322. **Quantitative determination of aluminium in special materials, especially magnetic alloys.** W. Dübel and W. Flurschütz (VEB Hartmetallwerke, Immelborn). *Chem. Tech., Berlin*, 1960, **12** (9), 538–540.—A rapid and accurate method is described for the determination of Al in alloys containing also ferro-magnetic metals (Fe, Co, Cr and Ni). It consists essentially in subjecting a soln. of the alloy to electrolysis with a special apparatus to effect complete separation of the ferro-magnetic metals, and then determining the Al in the separated soln., gravimetrically by pptn. as the 8-hydroxyquinoline complex.
H. L. Whitehead

2323. **Potentiometric measurement of the concentration of aluminium in solution in fused cryolite. I. Investigation and description of the measuring electrode.** M. Rolin and J. J. Gallay (Inst. Nat. des Sci. Appl., Lyon, France). *Bull. Soc. Chim. France*, 1960, (11–12), 2093–2096.—A preliminary study showed that the manipulation of oxygen electrodes is too complicated to give reliable results for the determination of Al in fused cryolite, and that, owing to the presence of molten aluminium, parasitic cells are inevitable. However, electrodes which are reversible with respect to the oxygenated anions can be prepared, using oxides which are only slightly soluble in mixtures of molten cryolite and aluminium.

Sintered rods of ferrosoferric oxide proved to be more satisfactory than those of ferric oxide from the point of view of reproducibility. Pure iron or molten aluminium can be used as auxiliary electrodes.

II. Experimental results. M. Rolin and J. J. Gallay. *Ibid.*, 1960, (11–12), 2096–2100.—Practical ways of setting up the cells are examined. In the final form, one half of the cell consists of a sintered rod of chromic oxide dipping into molten cryolite contained in a crucible of chromic oxide cast in a graphite case. Molten aluminium forms the second electrode and is situated in the base of the crucible, which is pierced at that point to give contact between the aluminium and the graphite case, which serves as conductor. A table of characteristic e.m.f. values, corresponding to various concn. of Al_2O_3 in the bath, is given. Temperature coeff. for e.m.f. were investigated. Chromic oxide and tin dioxide were preferred to ferric oxide and ferrosoferric oxide because of their superior mechanical and thermal properties.

III. Thermodynamic study of results. M. Rolin and J. J. Gallay. *Ibid.*, 1960, (11–12), 2101–2104.—A thermodynamic treatment is given of electrode reactions occurring when sintered rods of metal oxides are in contact with fused cryolite. It is shown that from the thermodynamic viewpoint such electrodes are analogous to silver - silver chloride or calomel electrodes in aq. soln.

J. R. Hudson

2324. **Volumetric determination of alumina in silicates.** I. A. Voinovitch and A. Lefranc-Kouba. *Chim. Anal.*, 1960, **42** (11), 543–548.—During work on the direct determination of Al_2O_3 in silicates, the technique described, claimed to be semi-direct, rapid and precise, was developed. The sample is made soluble by fusion with Na_2CO_3 - K_2CO_3 and the Si is determined by the usual technique. The filtrate is adjusted to be 1·5N with respect to HCl and cooled to ≃ 6° to 8°, then 6% aq. cupferron is added, 1 ml in excess. The pptd. Fe and Ti is collected and washed. To the filtrate is added 5 to 8 ml of $CHCl_3$ and by stirring for 5 min. the excess of cupferron is dissolved in the $CHCl_3$. Aluminium is determined in this soln. by addition of excess of EDTA, boiling for 10 min., cooling, and then back-titrating with $ZnCl_2$ soln. in the presence of dithizone. It is claimed that once the Al - EDTA complex is formed, the liberation of the cupferron on boiling is no longer detrimental to the volumetric finish. Some typical results on standard clays are given.

G. P. Mitchell

2325. **Determination of low concentrations of aluminium and chromium.** L. R. Pitwell (Dominion Magnesium Ltd., Plant Office, Haley, Ontario, Canada). *Analyst*, 1960, **85**, 849–850.—In the method previously described for determining traces of Al and other impurities (*Anal. Abstr.*, 1959, **6**, 1188), the Al is co-pptd. with a known amount of lanthanum carrier by aq. NH_3 and H_2O_2 and the ppt. is dried and ignited at 1000° and examined spectrographically. After several years' routine use, additional facts have been ascertained. Nitrate causes incomplete pptn. of La, so that $LaCl_3$ should be used, and NO_3^-, if present, should be removed. Quant. pptn. of the La is assisted by beginning the pptn. from a strongly acid soln. (30 ml of HCl) and then adding aq. NH_3. For large samples of magnesium (10 g), NH_4Cl (10 g) is also added. A permanent working graph can be plotted from the results obtained for triplicate samples. When 50 mg of La is used, the effective lower limit for a 10-g sample is 0·1 p.p.m. of Al. Chromium can be simultaneously determined to a lower limit of 0·05 p.p.m. by measuring the log of the intensity ratio of the Cr line at 2835·6 A to the La line at 2855·9 A.

A. O. Jones

2326. **Use of tritium tracer for the determination of hydrogen in aluminium.** A. S. Gillespie, jun. (Alcoa Res. Lab., Aluminum Co. of America, New Kensington, Pa.). *Anal. Chem.*, 1960, **32** (12), 1624–1626.—A solid extraction technique is used to extract the gas from the metal at a temp. near its m.p. Dry H is used as a carrier gas. The H and ^3H are collected in an ionisation chamber, and the ionisation current is measured by a vibrating-reed electrometer. Tritium activities of from 10^{-9} ($\simeq 3 \times 10^{-10}$ ml of H as pure ^3H) to 10^{-3} C can be measured. The method compares well with existing solid extraction techniques; it is more sensitive, and surface-gas corrections are unnecessary. Isotope effects are not observed in gas-content measurements with mixtures of H and ^3H, or for the reactions of tritiated water vapour with molten aluminium; these effects are found when tritiated water attacks aluminium powder at room temp.

H. A. Foner

2327. **Determination of gallium in rocks by neutron activation analysis.** D. F. C. Morris and M. E. Chambers (Brunel College of Technol., London, W.3, England). *Talanta*, 1960, **5** (3–4), 147–153 (in English).—Neutron activation converts the naturally occurring isotopes ^{69}Ga and ^{71}Ga into ^{70}Ga ($t_{\frac{1}{2}}$ = 21·1 min.) and ^{72}Ga ($t_{\frac{1}{2}}$ = 14·3 hr.). After irradiation, samples and standards are set aside to allow the ^{70}Ga to decay. Inactive Ga carrier is then added and the samples are dissolved in 40% HF. Pure Ga is isolated by ether extraction from 5·5N-HCl soln., contaminating elements are removed by scavenging with Sb and Fe, and the Ga is finally pptd. with 8-hydroxyquinoline and ammonium acetate. The ppt. are dried and their β-particle emissions counted. Decay curves are constructed and extrapolated to arbitrary times giving activity values for samples and standards from which the Ga content of the original material can be calculated. A sample known from many different analyses to contain 19 ± 3 p.p.m. of Ga gave results of 19·5 to 21·6 p.p.m. of Ga, and a second sample containing 17 ± 5 p.p.m. of Ga gave 17·5 and 18·4 p.p.m. Errors due to the formation of ^{72}Ga from Ge, As, Zn and U are negligible on normal rock samples.

W. T. Carter

2328. **Determination of indium and gallium by morin.** A. N. Busev and E. P. Shkrobot. *Vestn. Moskov. Univ., Ser. Matem., Mekhan., Astron., Fiz., Khim.*, 1959, (4), 199–206; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 77,038.—Small amounts of In and Ga can be determined as complexes with morin (**I**) by spectrophotometric or fluorimetric methods. Conditions for the spectrophotometric determination of In are—a pH of 3·6 (acetate buffer), a concn. of 5 to 100 μg of In per 10 ml, a concn. of **I** of $4·4 \times 10^{-4}$M, and a wavelength of 410 to 415 mμ (mol. extinction coeff. 24,400 to 16,000). The conditions for Ga are—pH 3·6, a concn. of 0·5 to 15 μg of Ga per 10 ml, a concn. of **I** of $2·6 \times 10^{-4}$M, and a wavelength of 450 to 420 mμ (mol. extinction coeff. 71,400 to 43,940). For the fluorimetric determination of In or Ga the

green fluorescence emanating from complexes with **I** in acetate buffer (pH 3·6) is measured. With a concn. of **I** of 4·4 × 10^{-5}M, 0·003 to 1 μg of In per 10 ml or 0·005 to 0·5 μg of Ga per 10 ml can be determined. The relative error of the spectrophotometric determination is < 10% and of the fluorimetric determination is < 20%. Both methods require a preliminary separation of In and Ga. Citric, tartaric, oxalic and sulphosalicylic acids cannot be used to mask In or Ga, as their complexes are more stable than the complexes of In or Ga with **I**. K. R. Cook

2329. **Spectrophotometric determination of indium with 1-(2-pyridylazo)-2-naphthol.** Shozo Shibata (Govt. Ind. Res. Inst., Nagoya, Japan). *Anal. Chim. Acta*, 1960, **20** (5), 434–438 (in English).—1-(2-Pyridylazo)-2-naphthol (PAN) forms a 2:1 complex with In, and in $CHCl_3$ this complex has a mol. extinction coeff. of 19,600 at 560 mμ. *Procedure*—To 20 ml of a neutral or slightly acid soln., containing ≃ 50 μg of In, add 1 ml of a 0·1% soln. of PAN in methanol, and 5 ml of acetic acid - Na acetate buffer soln. (pH 5·4 to 6·7). After 5 min. extract with 10 ml of $CHCl_3$, centrifuge the extract, determine its extinction at 560 mμ and derive the In content from a calibration graph. Citrate, tartrate, Fe, Zn, Cu and Ga interfere; Zn and Cu must be removed, but a correction for Fe can be calculated if the extinction due to its complex with PAN is determined at 775 mμ. H. N. S.

2330. **Detection of thallium.** I. M. Korenman, V. G. Ganina and R. P. Mashtakova. *Trudy Khim. i Khim. Tekhnol.*, 1959, (2), 376–379; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 77,039.—The detection of Tl is possible if it is first pptd. with HCl as TlCl and then completely co-pptd. with $PbCl_2$ by the addition of 1% $Pb(NO_3)_2$ soln. (0·1 ml). Both ppt. are dissolved in hot H_2O and separated from other insol. chlorides; Pb does not interfere with the microcrystalloscopic detection of Tl by reaction with $Na_2Pb[Cu(NO_2)_6]$; the detectable minimum is 0·12 mg of Tl in 0·5 ml of soln. Thallium may be separated by extraction with ether, during which Tl is oxidised with bromine or iodine; Tl^{3+} are detected by a spot test with benzidine (detectable minimum, 0·05 mg of Tl in 0·5 ml of soln.) or by microcrystalloscopic reaction with urea (detectable minimum, 0·12 mg of Tl in 0·5 ml of soln.). Other ions that may be present do not interfere; Au interferes in the fluorescence reaction with rhodamine B. K. R. Cook

2331. **Concentration of traces of thallium.** I. M. Korenman, P. A. Ganichev and I. A. Gur'ev. *Trudy Khim. i Khim. Tekhnol.*, 1959, (2), 397–400; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 77,040.—Thallium is co-pptd. with the bromination products of diaminoazobenzene (**I**); Tl^+ are oxidised by Br, with the formation of $(TlBr_4)^-$, which give practically insol. compounds with aromatic amines. Use of the radioactive isotope ^{204}Tl indicates that the amount of Tl being co-pptd. depends on its concn., the ratio of **I** to Br, the acidity of the medium and the rate at which the reagent is added. The most complete recovery of Tl is observed with a concn. of 0·0075 to 1·00 μg of Tl per 4 ml of soln. and with a ratio of **I** to Br of 1:1·25. Co-pptn. is carried out in 0·4N-HCl soln. with rapid addition of the reagent; Fe^{3+}, Pb^{2+}, Zn^{2+} and Cu^{2+} in 1000-fold amounts do not affect the co-pptn. of Tl. K. R. Cook

2332. **Determination of scandium in wolframite by activation analysis.** L. van Wambeke and G. Pinte (Centre Comm. de Rech., Euratom, Saclay, France). *Bull. Soc. Chim. France*, 1960, (11–12), 1901–1902.—Classical and spectrographic techniques for the determination of Sc in wolframite are tedious and complicated. The fluorescence method is not sufficiently sensitive to deal with the concn. of Sc encountered. Neutron activation produces ^{46}Sc which has half-lives of 20 sec. and of 85 days. The short-lived isotope cannot be used because of interferences from impurities; to use the longer-lived isotope, Sc must be separated from Fe, a suitable procedure being described. Details of the activation and of the comparison of the activities of the soln. obtained with those of standard soln. are given. The precision is quoted as 10 to 15% and the limit of sensitivity as 0·1 μg of Sc per litre. The method is recommended for the preparation of standard samples to be used in emission spectrography. J. R. Hudson

2333. **Determination of scandium in rocks and meteorites by neutron-activation analysis.** D. M. Kemp and A. A. Smales (A.E.R.E., Harwell, Berks., England). *Anal. Chim. Acta*, 1960, **23** (5), 410–418 (in English).—The Sc from the irradiated sample is finally isolated as its benzenesulphinate, which provides a suitable source for the measurement of ^{46}Sc by γ-spectrometry. Sufficient "cooling" time is allowed to prevent interference from ^{48}Sc. Interference from high proportions of Ti can be avoided or corrected for. The determinations cover the range 7·5 to 40 p.p.m. of Sc. H. N. S.

2334. **Determination of oxygen in yttrium and yttrium fluoride by the inert-gas fusion method.** C. V. Banks, J. W. O'Laughlin and G. J. Kamin (Inst. of Atomic Res., Iowa State Univ., Ames, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1613–1616.—A Leco oxygen analyser (No. 534–300) is used. The sample is placed in a graphite crucible heated by an induction furnace, and commercial Ar (for samples containing ≃ 1000 p.p.m. of O) is passed through the apparatus at 1·25 p.s.i. and 250 ml per min. The CO formed is passed through I_2O_5 and the CO_2 produced is measured conductimetrically in $Ba(OH)_2$ soln. Ascarite or asbestos coated with magnesium oxide is used in the absorption train during the analysis of yttrium fluoride to remove SiF_4, which is assumed to be formed. A special long graphite crucible is employed (*cf.* Kallmann and Collier, *Anal. Abstr.*, 1961, **8**, 2305). *Procedure*—For the blank, out-gas the crucible for 30 min. at 2600°, adjust the temp. to between 2100° and 2200°, and allow the crucible to cool for 5 to 10 min. Heat for 2 min. to the operating temp. and adjust the bridge to zero. Heat the crucible for a further 2 min., shut off the power, and sweep the system with gas for 4 min. Record the change in conductance. The blank should be ⩾ 2 ohms (≡ 35 μg of O). For calibration, use Ag_2O, or yttrium metal of known O content. Linear relationships are obtained between 100 and 400 μg of O. Wrap samples in platinum foil (3 times their own wt.) and process as for the blank. This method of treating the sample is superior to others tried. Results agree well with those obtained by other methods, except that the $KBrF_4$ method for yttrium fluoride gives consistently low results. H. A. Foner

2335. **Gravimetric determination of cerium(III) and cerium(IV), lanthanum, yttrium, uranium and titanium.** B. D. Jain and S. P. Singhal (Chem.

Dept., Univ., Delhi). *J. Sci. Ind. Res., India, B*, 1960, **19** (12), 494–495.—Ter- and quadri-valent Ce, La^{3+} and Y^{3+} (10 to 20 mg) can be completely pptd. from soln. (150 ml) by 2,5-dihydroxy-*p*-benzoquinone (**I**) (0·2 g) at pH 2·5 to 3·0; Ti^{4+} are completely pptd. by **I** at pH 0·8 to 1·5, while UO_2^{2+} can be completely pptd. by **I** at pH 2·8 to 7·0 in the presence of NH_4Cl; Fe^{3+} interfere with the determination of Ti^{4+}. In each case, the ppt. is filtered off, washed, dried and ignited, and the rare-earth element is weighed as oxide. Satisfactory recoveries are reported. The determination of Th and Zr by means of **I** has been previously described (*Anal. Abstr.*, 1960, **7**, 5202).

I. A. SIMPSON

2336. **Absorption spectra of molten fluoride salts: solutions of praseodymium, neodymium and samarium fluoride in molten lithium fluoride.** J. P. Young and J. C. White (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1658–1661.—A recording spectrophotometer with a high-temp. cell-assembly is used (*Ibid.*, 1959, **31**, 1892; 1960, **32**, 799). Measurements are taken at 900° with the molten salts (in the form of a pendant drop) contained in a platinum tube. The concn. of the rare-earth elements is determined spectrophotometrically. The molar absorptivity of each metal in soln. is less than in aqueous systems. H. A. FONER

2337. **Radiochemical precipitation studies of rare-earth oxalates.** K. G. Broadhead and H. H. Heady (Reno Metallurgy Res. Center, Bureau of Mines, U.S. Dept. of the Interior, Reno, Nev.). *Anal. Chem.*, 1960, **32** (12), 1603–1606.—A survey of the oxalate pptn. method for the determination of Y, La and Sm is given. Experiments on ^{90}Y, ^{140}La and ^{153}Sm were carried out to evaluate the effect of temp., digestion time, pH, rare-earth-metal concn., oxalic acid concn. and the presence of other rare-earth metals. A statistical treatment is given. General recommendations for minimising losses are—to keep rare-earth-metal concn. above 0·01M; to stir the reaction mixture for several minutes after pptn.; to use a two to five-fold excess of oxalic acid at $\simeq 0°$; to avoid excess of mineral acid; and (if possible) to keep the pH at 2. Complexing agents (*e.g.*, EDTA) interfere with the pptn. H. A. FONER

2338. **Three methods for the determination of total and organic carbon in geochemical studies.** I. C. Frost (U.S. Geol. Surv., Denver, Colo.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 480–483.—Outlines are given of the following procedures—(*i*) tube-furnace combustion with gravimetric determination of evolved CO_2; (*ii*) a gasometric method using fusion with Na_2O_2 in a closed bomb, with the addition of a combustion aid such as powdered magnesium or aluminium; and (*iii*) a modified combustion using a large sample (5 g), CO_2 being absorbed in $Ba(OH)_2$ soln. and the excess of $Ba(OH)_2$ being titrated with HCl. Method (*i*) is recommended for control purposes, (*ii*) for samples estimated to contain $> 0·5\%$ of organic carbon and (*iii*) for samples estimated to contain $< 0·5\%$. R. A. HOWIE

2339. **Determination of carbon dioxide in carbonate rocks by controlled loss on ignition.** O. K. Galle and R. T. Runnels (Kansas Geol. Surv., Lawrence, U.S.A.). *J. Sediment. Petrol.*, 1960, **30** (4), 613–618.—The routine method for loss on ignition is modified to include the loss at 550° as well as at 1000°, so that values are obtained for the carbonate and non-carbonate portions. *Procedure*—Grind the sample to pass a 60-mesh sieve. Weigh a 2-g portion into a platinum crucible and dry for 1 hr. at 105°; record the weight. Place the sample in a muffle-furnace at 550° for exactly 25 min., remove, cool and weigh, and record the loss. Return the sample to the muffle-furnace and increase the temperature to 1000°, leave at 1000° for 1 hr., remove, cool and weigh, and record the CO_2 lost. For an argillaceous limestone standard (U.S. Bur. Standards 1a), the mean deviation for CO_2 was 0·10%, and for total loss on ignition 0·04%. R. A. HOWIE

2340. **Combination of gravimetric and spectrographic methods in the analysis of silicates.** R. E. Stevens, A. A. Chodos, R. G. Havens, E. Godijn and S. T. Neil (U.S. Geol. Surv., Menlo Park, Calif.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 499–501.—Precipitates and other separated residues obtained in a system of wet chemical separations were analysed spectrographically. The procedures described aim at the measurement of all non-volatile constituents, correction of the weight of each ppt. or residue for material other than the constituent sought, correction of each determination for the quantity of the constituent which failed to separate, and correction of each determination for materials added in reagents, filter-paper and airborne dust by a blank analysis.

R. A. HOWIE

2341. **Pulse generators for excitation of spectra, and their use for the quantitative analysis of silicates.** É. E. Valnshtein and V. V. Korolev (V. I. Vernadskii Inst. for Geochem. and Anal. Chem., USSR Acad. Sci., Moscow). *Chim. Anal.*, 1960, **42** (10), 479–489.—A circuit diagram is given. By using ^{64}Cu it is shown that the distribution of atoms and ions in the space between the electrodes is more uniform for pulse excitation than for continuous arc or spark excitation. It is also shown that the temp. obtained in pulse excitation are higher than in the continuous arc. The uniformity of distribution of atoms and ions and the high temp. in the pulsed arc improve the precision (*e.g.*, the difference between the densities of the 5889·9 Å Na line and the 5700·2-Å Cu line is not altered by wide changes in current density and inter-electrode distance). The use of the pulsed arc made possible the simultaneous determination of SiO_2 (10 to 80%), TiO_2 (0·1 to 2·5%), Al_2O_3 (0·5 to 40%), Fe_2O_3 (0·5 to 40%), CaO (0·5 to 50%), MgO (0·01 to 40%), MnO (0·01 to 20%), K_2O (0·5 to 14%) and Na_2O (0·5 to 12%) in a number of silicate rocks. Under the given conditions the coeff. of variation was $\simeq 3\%$ for each element. E. M. ROWLEY

2342. **Neutron-activation analysis of halogens in high-purity silicon.** Tadashi Nozaki, Toshi Kawashima, Hideo Baba and Hidemaro Araki (Electrical Communication Lab., Musashino, Tokyo). *Bull. Chem. Soc. Japan*, 1960, **33** (10), 1428–1430 (in English).—Samples (0·5 to 1·0 g) were irradiated for 1 hr. in a flux of 6×10^{11} neutrons per sq. cm per sec., then fused with KOH (10 to 15 g) containing NaCl, KBr and KI (5 to 10 mg each) as carriers; the melt was cooled, dissolved in H_2SO_4, and transferred to a distillation apparatus; bromine, chlorine and iodine were distilled off successively after the addition of CrO_3. The separated halogens were then reduced, pptd. as the silver salts and

counted with an end-window Geiger-Müller counter. The lower limits of detection are $1{\cdot}5 \times 10^{-7}$ g of Cl, $1{\cdot}5 \times 10^{-8}$ g of Br and $3{\cdot}0 \times 10^{-8}$ g of iodine. T. R. ANDREW

2343. **Ion-exchange separation of germanium.** T. R. Cabbell, A. A. Orr and J. R. Hayes (Pennsylvania State Univ., Univ. Park, Pa.). *Anal. Chem.*, 1960, **32** (12), 1602–1603.—A mixed resin bed composed of Nalcite HCR, 8% cross-linked, 50 to 100 mesh (**I**), and Amberlite IR-45 (**II**) is used. It is necessary to wash **I** with 6N-HCl and then with water (to remove Fe) before use. A fresh column (7 g of **I** mixed with 3 g of **II**) is employed for each separation, and the pH of the sample soln. added must be $\simeq 2$. The Ge in the percolate is determined by the photometric phenylfluorone method (Luke and Campbell, *Anal. Abstr.*, 1957, **4**, 65). No interference is given by Sb^{III}, As^{III}, Mo^{VI}, Ca, Mg, Pb, Ag, Cr^{III}, Ni, Bi, Sn^{IV}, Zn or Fe^{III} in amounts up to at least fifteen times the wt. of Ge; Ti and W interfere. The method was applied to the analysis of coal with a known amount (0·3 mg) of Ge added. H. A. FONER

2344. **Photometric determination of tin by means of catechol violet.** V. P. Sagakova and A. I. Lyubivaya. *Trudy Ukr. Nauch. Inst. Konserv. Prom.*, 1959, (2), Pt. 1, 118–123; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 77,044.—Quadrivalent Sn forms a complex with catechol violet (**I**) having a max. extinction at 620 mμ (pH 3 to 5). The ratio of Sn to **I** in the complex is 2:3. To determine Sn, add to the test soln. 20% NaCl soln. (2·5 ml), acetate buffer (pH 3 to 5), 1% gelatin soln. (0·5 ml) to stabilise the colour, and 0·1% ethanolic **I** soln. (0·5 ml), dilute to 10 ml, set aside for 10 min. and measure the soln. photometrically in a 10-mm cell, with a red filter. Use a control as the comparison soln. The minimum determinable amount of Sn is 0·5 μg. An error $< 5\%$ is obtained with 1 to 4 μg of Sn. The presence of 500 to 1000 mg of K, Na or Ca, 250 mg of P, 4 mg of Cu, or 3 mg of Fe does not affect the determination. K. R. COOK

2345. **Volumetric determination of lead with alkali ferrocyanides in the presence of 3,3′-dimethylnaphthidine.** H. Basińska and K. Przybyszewska (Copernicus Univ., Toruń, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 535–540.—Neutral or slightly acid soln. of Pb^{2+} can be titrated with lithium, sodium or potassium ferrocyanide, with 3,3′-dimethylnaphthidine as indicator, provided that a trace of ferricyanide is present. Aliquots of 0·1M-Pb acetate containing up to 0·5 g of Pb gave reproducible results about 0·3% high with $Li_4Fe(CN)_6$ and $Na_4Fe(CN)_6$ and about 0·8% high with $K_4Fe(CN)_6$. The end-point (red to green) is sharp and is not affected by the addition of ethanol or glacial acetic acid up to equal vol. or by acidification with HNO_3 up to 0·5N. P. BRYCH

2346. **Determination of lead in zircon with dithizone.** F. Cuttitta and J. J. Warr (U.S. Geol. Surv., Washington, D.C.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 486–487.—A finely ground sample (0·1 g, containing 8 to 15 μg of Pb) is fused with an equal proportion of Na_2CO_3 and sodium borate and the melt is dissolved in HNO_3 (3:7) (15 ml) and water (20 ml). The Pb is extracted as the dithizone complex with $CHCl_3$ and determined spectrophotometrically. R. A. HOWIE

2347. **Determination of lead in iron-bearing materials.** J. J. Warr and F. Cuttitta (U.S. Geol. Surv., Washington, D.C.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 483–484.—A sample containing approx. 15 μg of Pb is dissolved in aqua regia (10 ml) and HF (5 ml) in a Teflon beaker on a steam bath, and the salts are converted into chlorides by evaporation to dryness several times with HCl. The chlorides are dissolved in N-HCl (25 ml) and the soln. is cooled to 5° to 10°, transferred to a 125-ml separating-funnel together with cupferron (0·5 g) and cold $CHCl_3$ (20 ml), shaken for 2 min. and the lower layer is separated. The acidity of the aq. phase is increased to 1·5N by adding 6N-HCl (3 ml), 1% diethylammonium diethyldithiocarbamate soln. in $CHCl_3$ (10 ml) is added, the soln. is shaken for 1 min. and the carbamate layer is separated and evaporated nearly to dryness. The organic matter is destroyed with conc. HNO_3 (3 ml) and $HClO_4$ (0·5 ml), the soln. is evaporated to dryness, and the residue is dissolved in HNO_3 (1:1) (1 ml) and water (5 ml). Lead is determined spectrophotometrically by the dithizone procedure, with $CHCl_3$ as solvent. R. A. HOWIE

2348. **Determination of lead in pyrites.** F. Cuttitta and J. J. Warr (U.S. Geol. Surv., Washington, D.C.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 485–486.—The separation and purification of pyritic lead for chemical or mass-spectrometric analysis (for geochronological studies) is described. Lead is separated from large quantities of Fe by means of a sulphide pptn. in which Cu acts both as a carrier for the PbS and as a catalyst for the reduction of Fe with hydroxylamine at pH 0·4 to 0·5. The Cu carrier and any Bi and Sn present are separated by re-pptn. as sulphides from 1·5M-HCl, and Pb is then extracted from the soln. with 1% diethylammonium diethyldithiocarbamate soln. in $CHCl_3$. The organic matter in the extract is destroyed and the Pb is again isolated and determined with dithizone. Details are also given for the preparation of PbI_2 for mass spectrometry. R. A. HOWIE

2349. **Separation of lead from molybdenum by the deposition method.** N. K. Podberezskaya. *Trudy Kazakh. Nauch. Inst. Mineral. Syr'ya*, 1959, (1), 199–204; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 77,006.—The photometric determination of Mo with thiocyanate is affected by the presence of Pb, which is pptd. as thiocyanate; Pb can be quant. separated from Mo by deposition on aluminium metal by boiling in alkaline soln. Fuse the ore (1 to 2 g) with alkali (5 g) in an iron dish. Add hot H_2O and H_2O_2 (5 drops) to the melt, boil for 5 min., then dilute with H_2O to 250 ml. To a 20-ml aliquot add aluminium wire (diam. 2 mm) (2 g) and boil for 15 min. Filter off the residue and wash ($\times$ 5 or 6) with hot H_2O. Determine Mo photometrically in the filtrate. Satisfactory results were obtained in the determination of Mo (0·022 to 0·32%) in standard samples to which Pb (0·05 g) had been added. K. R. COOK

2350. **Preparation of lead iodide for mass spectrometry.** F. Cuttitta and J. J. Warr (U.S. Geol. Surv., Washington, D.C.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 487–488.—The isotopic composition of lead isolated from mineral samples is the basis for many geological-age determinations. Details are given for the preparation of PbI_2 from pure galena, from pure or impure $PbSO_4$ occurring

as a natural mineral, or by H_2SO_4 attack on some minerals, and from uranium-bearing materials, felspars and zircons. R. A. HOWIE

2351. **Potentiometric determination of bi- and ter-valent titanium.** L. Giuffrè and F. M. Capizzi (Milan Polytech., Italy). *Ann. Chim., Roma*, 1960, **50** (8–9), 1150–1157.—The sum of Ti^{2+} and Ti^{3+} is determined by potentiometric titration of a soln. or suspension of the sample in anhyd. methanol, in an inert atmosphere at $-15°$ to 0°, with a standard soln. of $FeCl_3$ in anhyd. methanol. Indirect methods of deriving the individual contents of Ti^{2+} and Ti^{3+}, when both are present, are indicated. L. A. O'NEILL

2352. **Quantitative determination of titanium with EDTA.** W. Lieber (Portland-Zementwerke, Heidelberg, Germany). *Z. anal. Chem.*, 1960, **177** (6), 429–430 (in German).—If Ti^{4+} are oxidised with H_2O_2 to TiO_2^{2+} and titrated with EDTA in the presence of a known amount of Fe^{3+}, the titre gives the sum of Fe and Ti. Salicylic acid is used as indicator, preferably with photometric determination of the end-point. Aluminium, Ca, Mg and alkali metals do not interfere, and the accuracy is good. P. D. PARR-RICHARD

2353. **Polarographic determination of titanium in red iron oxide.** J. Stabryn (Moravské Chemické Závody, Ostrava, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (11), 584–585.—After dissolving the sample, Fe is quant. removed by extraction with ethyl ether from HCl soln., and Ti is determined polarographically in ammonium acetate soln. J. ZÝKA

2354. **Determination of zirconium with benzoylphenylhydroxylamine.** D. E. Ryan (Dalhousie Univ., Halifax, Nova Scotia, Canada). *Canad. J. Chem.*, 1960, **38** (12), 2488–2492.—The pptn. of Zr from HCl and H_2SO_4 soln. with *N*-benzoyl-*N*-phenylhydroxylamine (**I**) was investigated. The ppt. from 0·5N-H_2SO_4 can be dried at 110° and weighed, but the ppt. from 0·5N-HCl may contain basic salts of lower mol. wt., and must therefore be ignited to ZrO_2. *Procedure for direct weighing*—To 100 to 150 ml of Zr soln. in H_2SO_4 (> 0·5N) add dropwise, with stirring, a slight excess (> 40 mg in excess per 100 ml) of **I** (4% in 95% ethanol). Digest for 1 hr. on a steam bath and filter off and wash the ppt., first with cold H_2O, then with hot H_2O (3 × 5 ml, 80°) and dry at 110°. The factor is 0·0970. Tin, V^V, Ce^{IV} and Ti interfere, but Cu^{II}, Al, Bi, Cd, Cr^{III}, Pb, Mg, Mn^{II}, Ni, Zn, UO_2^{2+}, Th^{IV} and the rare-earth metals do not; Fe^{III} forms a soluble purple complex. Zirconium is not pptd. in the presence of F^-. Determinations of 8 to 25 mg of Zr were accurate to ± 0·04 mg; 0·1 mg of Zr per 100 ml can be detected, and 0·2 mg can be determined. C. S. HOWES

2355. **Complexometric titration of zirconium with 4,5-dihydroxy-3-(4-sulphophenylazo)naphthalene-2,7-disulphonic acid.** Sachindra Kumar Datta. *Chim. Anal.*, 1960, **42** (11), 562–564.—This dye (SPADNS) is used as an indicator in the direct titration of Zr with EDTA; the colour change at the end-point is from reddish-brown to yellow. The effect of pH, temp. and extraneous ions and the stoicheiometric nature of the reaction are investigated. Thorium is also stoicheiometrically titrated under the same conditions. G. P. MITCHELL

2356. **Determination of zirconium in niobium alloys [by means of EDTA and amperometric titration of the excess].** Yu. A. Chernikhov and V. M. Vladimirova. *Zavod. Lab.*, 1960, **26** (11), 1207–1208.—With contents of Zr of < 2%, the sample (0·3 g) is dissolved in 20 ml of HNO_3 (1:1) and a few ml of HF in a platinum dish. After addition of 15 ml of H_2SO_4 (1:1), the soln. is evaporated to the formation of moist sulphates, and then fused with 2 g of $KHSO_4$. The melt is dissolved in 20% tartaric acid soln. and diluted with the same soln. to 50 ml. An aliquot (5 to 10 ml) is boiled for 1 to 2 min. with 10 ml of HCl (1:1), then diluted to ≃ 40 ml with water (any cloudiness that has appeared during the treatment with HCl should disappear) and treated with 1 g of ammonium acetate, an excess of 0·01M-EDTA and 2 to 3 drops of Tropaeolin OO (C.I. Acid Orange 5) soln., followed by neutralisation with aq. NH_3 to pH 2 (pinkish-yellow colour). With contents of Zr of ≃ 4%, an aliquot (5 to 10 ml) is treated with 5 to 10 ml of the EDTA soln. The excess of EDTA is titrated amperometrically with a 0·01M soln. of Bi at 0·3 V. With contents of Zr of < 2%, the sample (0·5 to 1 g) is ignited to oxides and fused at 900° to 1000° with six times their weight of K_2CO_3. The cooled melt is heated with 60 to 70 ml of water and the soln. is filtered through paper pulp. The insoluble matter is washed with 2% K_2CO_3 soln. and ignited. The residue is fused with 1 to 2 g of $KHSO_4$ and the cooled melt is dissolved in 25 to 50 ml of 10% tartaric acid soln. The subsequent procedure is as described above. G. S. SMITH

2357. **Determination of oxygen in zirconium by the platinum-flux technique.** C. Venkateswarlu and M. W. Mallet (Battelle Mem. Inst., Columbus, Ohio, U.S.A.). *Talanta*, 1960, **5** (3–4), 283–287 (in English).—The method of Hansen *et al.* (*cf. Anal. Abstr.*, 1960, **7**, 936) is applied to zirconium. The recommended experimental conditions are a 0·1-g sample, a flux to sample ratio of 5:1 and extraction for 20 min. at 1900° to 1950°. Twelve analyses of a sample containing 0·131% of O gave a standard deviation of 0·0038%. W. T. CARTER

2358. **Determination of oxygen in zirconium and Zircaloy by the inert-gas fusion method.** P. Elbling and G. W. Goward (Bettis Atomic Power Lab., Westinghouse Electric Corp., Pittsburgh, Pa.). *Anal. Chem.*, 1960, **32** (12), 1610–1613.—The sample is fused with > 7 times its own wt. of platinum in an induction-heated graphite crucible. Purified Ar is used as carrier gas, and the CO formed is oxidised by I_2O_5 to CO_2, which is determined conductimetrically. Before use the crucible is out-gassed for 30 min. at 2500° to 2600° at a gas-flow rate of 0·35 litre per min. All determinations are made at ≃ 2100°. The apparatus is calibrated with U_3O_8, Ag_2O, ZrO_2 or Nb_2O_5 (with a reaction time of 10 min.). The blank should be > 2·0 μg of O per min. The plot of O content *vs.* corrected reading is linear up to 700 μg of O. Oxide coating and grease are removed from the sample (0·1 to 0·3 g), which is wrapped in platinum foil and treated in the same way as the oxide standards. Investigation shows that the Pt to Zr ratio must be > 7:1. Analysis of standard samples of oxygenated Zr shows that recovery is quantitative in the range 900 to 3700 p.p.m. The coeff. of variation of the method is ≃ 6%. H. A. FONER

2359. **Determination of alkali metals and halides in zirconium dioxide by means of high-voltage electro-dialysis.** S. V. Elinson and A. T. Rezova. *Zavod. Lab.*, 1960, **26** (11), 1209–1210.—The dialyser (glass, quartz or Plexiglas) consists of three chambers separated by Cellophane diaphragms. The end chambers contain gauze or sheet-platinum electrodes. The middle chamber contains a suspension of the impure ZrO_2 in water and the outer chambers contain water. Voltages up to 2000 V and currents up to 300 mA can be obtained. Dialysis is continued until the current becomes very small. The cathodic and anodic liquids are run out into measuring flasks and replaced by water. The dialysis is continued until the current again becomes small. The cathodic and anodic liquids are run into the measuring flasks and replaced with water if the dialysis is to be continued. The content of K in the cathodic liquid is determined gravimetrically by the tetraphenylborate method and the content of F in the anodic liquid is determined colorimetrically or as PbClF. The method gave satisfactory results for K between 1·25 and 10% and for F between 0·03 and 3%.

G. S. SMITH

2360. **Separation of zirconium and hafnium by extracting their nitrates with di-isoamyl methylphosphonate.** G. A. Yagodin, O. A. Mostovaya and A. M. Chekmarev. *Izv. Výssh. Ucheb. Zavedenií, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 135–137; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 77,007.—A study is made, with ^{95}Zr and ^{181}Hf, of the effect of various factors on the extraction of nitrates of Zr and Hf from HNO_3 soln. by 10% di-isoamyl methylphosphonate (**I**) in *o*-xylene (soln. of **I** in xylene satd. with HNO_3, at the same concn. as the soln. being extracted). It is established that HNO_3 facilitates the transference of both elements to the organic phase, and that the relation between the partition coeff. and the HNO_3 concn. is the same as with an extraction by tributyl phosphate, but the absolute value of the partition coeff. is somewhat higher. The partition coeff. of Hf rises more sharply than the coeff. of Zr with an increase in HNO_3 concn. The partition coeff. of Zr and Hf reach their maxima with extraction from 4N-HNO_3. An increase of the **I** concn. in *o*-xylene sharply increases the coeff. of both metals. Partial substitution of HNO_3 by $NaNO_3$ slightly affects the coeff. of Zr and Hf, and an increase in their concn. leads to a decrease in their partition coeff. With extraction of Zr and Hf from HCl soln., the coeff. are much lower than with HNO_3 (practically no Zr is recovered from 4N-HCl); Zr and Hf can be re-extracted from the organic layer with H_2O; re-extraction is increased if the temp. is raised to 50° and also by the addition of Na_2SO_4 (with a ratio of vol. of H_2O to the organic phase of 1:4, there is complete re-extraction of Zr and Hf).

K. R. COOK

2361. **Precipitation of metal 8-hydroxyquinolinates from homogeneous solution. II. Thorium.** Kazuyoshi Takiyama, E. D. Salesin and L. Gordon (Dept. of Chem. and Chem. Engng, Case Inst. of Technol., Cleveland, Ohio, U.S.A.). *Talanta*, 1960, **5** (3–4), 231–237 (in English).—In a comparison of the pptn. of Th with 8-hydroxyquinoline (**I**), either by direct addition of **I** or by generation of **I** from 8-acetoxyquinoline, it was found that the use of 8-acetoxyquinoline at 50° in the pH range 5·0 to 6·0 gives a ppt. with superior physical properties and improves the separation from Ce^{III}. A study of the methods of determining Th 8-hydroxyquinolinate indicated that accurate results could only be obtained by drying the ppt. at 180° ± 5° or by ignition to ThO_2. The bromination method is not recommended unless the ppt. is first dried at 180° ± 5°.

W. T. CARTER

2362. **Colorimetric determination of thorium in niobium-containing materials by means of arsenazo III.** V. M. Vladimirova and N. K. Davidovich (State Sci. Res. Inst. of the Rare-Metals Industry). *Zavod. Lab.*, 1960, **26** (11), 1210–1212.—*Determination of Th in niobium chlorides*—The sample (0·1 g) is dissolved in 4% ammonium oxalate soln., the soln. is diluted with a further amount of the same reagent soln. to 50 or 100 ml, and an aliquot (1 to 5 ml) is diluted to 20 ml with 4% ammonium oxalate soln., then treated with 12·5 ml of conc. HCl and 2 ml of 0·1% arsenazo III soln. [3,6-di-(*o*-arsonophenylazo)-4,5-dihydroxynaphthalene-2,7-disulphonic acid] and diluted to 50 ml with water. The extinction is measured with a red filter, and the content of Th is calculated by use of a calibration curve. Satisfactory results were obtained over the range 0·006 to 1·5%. *Determination of Th in niobium hydroxide and pentoxide*—The sample (0·1 to 0·2 g) is fused with 2 to 3 g of $KHSO_4$ at 500° to 600°, the cooled melt is dissolved in 4% ammonium oxalate soln., and the soln. is treated as described above. *Determination of Th in pyrochlore*—The sample (0·1 g) is dissolved in 10 ml of HF, the soln. is evaporated to dryness, a further amount (5 ml) of HF is added, and the soln. is again evaporated to dryness. The residue is treated with 10 ml of H_2SO_4 (1:1) and the soln. is heated to fuming. After addition of 5 ml of H_2SO_4 (1:1), the soln. is evaporated to dryness, the residue is dissolved in 50 ml of HCl (1:1), and the soln. is diluted to 100 ml with water. An aliquot is treated as described above. *Determination of Th in low concn.*—The sample (1 to 2 g) is dissolved in 10 to 15 ml of HF, the soln. is evaporated to dryness, and the residue is treated with 5 ml of HF and 50 to 60 ml of water. After addition of 15 to 20 mg of Ca as collector, the soln. is set aside for 2 hr. The ppt. is collected and washed with 5% HF soln. and ignited. The residue is evaporated twice with H_2SO_4 to remove F. After dissolution in HCl (1:1) a suitable aliquot is taken for the colorimetric determination.

G. S. SMITH

2363. **Spectrophotometric determination of thorium with Eriochrome black T. Ethylenedinitrilotetra-acetic acid and 2,2′,2″-nitrilotriethanol [triethanolamine] as masking agents.** P. F. Lott, K. L. Cheng and B. C. H. Kwan (Sch. Mines and Metall., Univ. Missouri, Rolla, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1702–1704.—Thorium and Eriochrome black T (**I**) form a red complex (molar absorptivity 35,000). The extinction is measured at 700 mμ (sensitivity, 0·004 μg of Th per sq. cm per 0·001 absorption unit). Few ions interfere and the effect of most of these is removed by the use of an aq. soln. containing 3·72% of EDTA (disodium salt) and 1·5% of triethanolamine. Iron interferes and is removed by extraction or pptn. as sulphide; Zr does not interfere if readings are taken within 15 min. of colour development; and the addition of hydroxyammonium chloride prevents interference from oxidising agents, *e.g.*, Ce^{IV}, V^{V} and U^{VI}. Determinations are carried out at pH 9 to 9·5. **I** and the Th - **I** complex are stable for a few hours at 100°.

H. A. FONER

2364. **Determination of thorium by means of X-ray fluorescence spectrography.** M. L. Borlera (Ist. Chim. Gen. e Appl. e Metallurg. Politecnico, Torino, Italy). *Ric. Sci.*, 1960, **30** (11), 1723–1725.—A Norelco spectrograph equipped with a tungsten anti-cathode X-ray tube at 50 kV and 30 mA is used. Calibration curves are prepared (*i*) with mixtures containing 0·2 to 1% of Th and 1% of an internal standard (U_3O_8 or HgO) to cover the range in Th-containing sands and (*ii*) with 2 to 5% of Th and 5% of internal standard for minerals containing more Th. The ratios of the intensities of the L_{α_1} and L_{α_2} radiations from the Th to those of the internal standard are plotted against concn. of Th, and the ratios obtained for the unknown are referred to the curve. If necessary, the samples may be diluted by grinding with Na_3PO_4 or SiO_2. With HgO as internal standard the error is $> 4\%$ for 1·5% of Th, and 2% for 5 to 10%. With U_3O_8 as internal standard the error is $< 0{\cdot}5\%$. The time required for a determination is 1 hr. The $L\beta$ line of Bi and the K_{β_2} line of Ge may interfere if these elements are present.

J. I. M. Jones

2365. **Analysis of gaseous mixtures containing mainly nitrogen oxides by mass spectrometry.** J. Tranchant and M. Moreau. *Mém. Poudres*, 1960, **42**, 445–456.—A mass spectrometer, type CEC 21–620, with a tungsten filament, is used for the analysis of gas mixtures containing N, N_2O, NO and NO_2, and mixed sometimes with H, H_2O, CO, CO_2 and hydrocarbons. The tungsten filament is conditioned with NO_2 or butane to give a coating of oxide or carbide, respectively. The gaseous mixture is then passed into the spectrometer and the peaks are measured and compared with standard curves. Explosives were burnt in a bomb calorimeter, and the evolved gases analysed similarly. The error is 3% for simple mixtures, and $\simeq 4\%$ for more complex mixtures. Full details are given of the preparation of pure samples of each of the oxides of N, and of CO, for the standard curves.

R. A. Hendey

2366. **Differential colorimetric determination of nitrite and nitrate ions.** J. L. Lambert and F. Zitomer (Dept. of Chem., Kansas State Univ., Manhattan, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1684–1686.—A red dye is formed by the diazotisation - coupling reaction. The amine used is *p*-aminophenyltrimethylammonium ion (**I**) in 1% soln. as the hydrochloride (prep. described), and the coupling agent is *NN*-dimethyl-1-naphthylamine (**II**) (in 1% HCl). Nitrite is determined directly in acid soln. Nitrate is reduced by zinc in ammoniacal soln. (pH = 10·8) in the presence of manganous hydroxide, and the NO_3^- formed are determined as before. The colour is stable for at least a week, has a molar absorptivity of 26,200 and is measured at 522 mμ. Any NO_3^- present during the determination of NO_2^- can be removed after diazotisation, by adsorption on the potassium form of a nuclear sulphonic cation-exchange resin (Amberlite IR-120). Residual Cl is removed from the test soln. by adsorption on the same resin. The soln. of **I** (stored in the dark) is stable for 6 months. The soln. of **II** should be prepared daily. Ranges covered are 0 to 1·5 p.p.m. of NO_2^- and 0 to 2 p.p.m. of NO_3^-.

H. A. Foner

2367. **I. Analysis of nitrate - nitrite mixtures. II. Experiments concerning the reduction of nitrate to nitrite.** G. Meerman. *Dissert. Abstr.*, 1960, **20** (12), 4507.—Nitrate and NO_2^- can be determined by their u.v. absorptions at 302 mμ and 353 mμ, directly if the NO_2^- concn. is $>$ one-half of the NO_3^- concn., and after destruction of NO_2^- by sulphamic acid for higher concn. Results from the volumetric and spectrophotometric methods are similar. A concn. of $< 0{\cdot}01$M in NO_2^- and 0·04M in NO_3^- is required. The error for the spectrophotometric method is $< 1\%$. Investigation shows that the quantitative reduction of NO_3^- to NO_2^- is not practicable.

O. M. Whitton

2368. **Precise determination of traces of pyrophosphate in orthophosphates.** R. H. Kolloff, H. K. Ward and V. F. Ziemba (Monsanto Chemical Co., St. Louis, Mo., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1687–1690.—The method described is based on the reduction in colour intensity of the ferric - thiocyanate complex in the presence of pyrophosphate. It is claimed to be 5 to 10 times as precise and 10 times as sensitive (0·002% of pyrophosphate per 0·001 extinction unit) as previous methods (Karl-Kroupa, *Ibid.*, 1956, **28**, 1091; Chess and Bernhart, *Ibid.*, 1958, **30**, 111) and is particularly suitable for routine analyses of soln. of the same general composition. Corrections can be made for the effect of Fe, Al and orthophosphates. The following ions interfere—cations that interfere with the ferric - thiocyanate system; anions that complex Fe (*e.g.*, polyphosphates); and cations that form complexes with pyrophosphate (Mg^{2+}, Al^{3+}, Ca^{2+}). The final soln. must be made up in low-actinic glassware, and the extinction is read at 435 mμ between 10 and 30 min. after its preparation. Readings must be taken at const. temp.

H. A. Foner

2369. **Rapid method for the estimation of phosphorus in coal.** S. S. Roy and S. Gupta (Central Fuel Res. Inst., Jealgora). *J. Sci. Ind. Res., India, B*, 1960, **19** (12), 495–496.—*Procedure*—Coal ash (0·5 g) is digested slowly to white fumes in a Pyrex-glass beaker with a mixture of conc. H_2SO_4 (3 ml), conc. HNO_3 (10 ml) and conc. HCl (15 ml). A smaller sample (0·2 g) is taken if the P content exceeds 0·15%. After dilution with H_2O to 200 ml, the soln. is boiled and filtered and P is pptd. from the filtrate as ammonium molybdophosphate by a modification of B.S. method No. 1016 (1942) and determined by dissolution of the ppt. in standard alkali and back-titration with HNO_3. Recoveries in 5 determinations agreed well with those by the B.S. method. The method is claimed to be simple, rapid and accurate, and needs no platinum ware.

I. A. Simpson

2370. **Photometric determination of phosphorus in tungsten ores.** C. Winterstein. *Z. Erzbergb. Metallhüttenw.*, 1960, **13** (11), 546–549.—The P is pptd. as $AlPO_4$ after a separation from W, and is determined photometrically after reaction with ammonium vanadate and molybdate. *Procedure*—The ore (2·5 g) is fused with Na_2CO_3 - K_2CO_3 and the melt is leached with water. After dilution to 500 ml, 200 ml is filtered off and carefully acidified with HNO_3 (1:1) so that no WO_3 is pptd. The CO_2 is boiled off, the soln. is cooled and 5 g of NH_4NO_3 and 25 ml of $Al_2(SO_4)_3.K_2SO_4$ soln. (2·5%) are added. The soln. is neutralised with aq. NH_3 (0·91), a 3-ml excess is added and the soln. is boiled and allowed to cool; the cold soln. is neutralised with HNO_3 (1:1) then made alkaline with 2 or 3 drops of aq. NH_3. The soln. is boiled, set aside,

and filtered. The ppt. is washed with weakly ammoniacal NH_4NO_3 soln. (5%) and dissolved in hot HNO_3. After the addition of 5 g of NH_4NO_3, the pptn. with aq. NH_3 is repeated. The filter is then ignited in a platinum crucible at as low a temp. as possible, and the residue is dissolved by evaporation with 10 ml of H_2SO_4 (1:1) and HF. The residue is leached with water, treated with H_2SO_3 and then 10 to 16 ml of aq. Br, and the soln. is evaporated to fumes to remove As. The aluminium salts are dissolved in water, leaving some ppt. of WO_3. After the addition of 10 g of NH_4NO_3, a further pptn. with aq. NH_3 is made, and the ppt. is dissolved in a little HNO_3. The soln. is evaporated almost to dryness and neutralised with aq. NH_3. Then 3 to 3·5 ml of HNO_3 (1:1) is added, followed by 10 ml of ammonium vanadate soln. (0·2345% of NH_4VO_3 in 1% aq. HNO_3) and 5 to 6 ml of H_2O_2 (3%). The soln. is boiled for 15 to 20 min., cooled and filtered, and the filter is washed with cold water. Then 10 ml of ammonium molybdate soln. (10%) is added and the soln. is diluted to 200 ml. After 20 min., the extinction of the soln. is measured (Eppendorf photometer, Hg filter 436) against that of a reagent blank. The preparation of the calibration curve is described. J. H. WATON

2371. **Analysis of phosphorus trichloride and phosphoryl chloride mixtures.** F. G. Stanford (Radiochem. Centre, Amersham, Bucks., England). *J. Chromatography*, 1960, **4** (5), 419 (in English).—The following conditions have been established for the separation of PCl_3 and $POCl_3$ on a Griffin and George Mk. II gas chromatograph with katharometer detection—a column (6 ft. × 0·25 in.) containing 23% (w/w) of silicone E301 on 80 to 120-mesh Celite 545; temp. 63°; carrier gas 1·75 litres of N per hr.; inlet pressure 63 cm, outlet 24 cm; bridge current 100 mA. The detector sensitivity is set at × 0·25. G. BURGER

2372. **Determination of micro amounts of impurities in high-purity antimony by means of radioactivation analysis.** É. E. Rakovskiĭ, L. A. Smakhtin and Yu. V. Yakovlev (V. I. Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1960, **26** (11), 1199–1200.—To determine traces of P, Cr, Mn, Cu, Zn, Ga and As in zone-refined antimony, the sample (100 mg) is irradiated for 20 to 48 hr. with neutrons ($8·7 \times 10^{13}$ per sq. cm per sec.) and dissolved in aqua regia (for the determination of Mn, Cr, Zn and Ga) or in Br - HBr (for the determination of Cu, P and As). Chromatographic and chemical separations are carried out, followed by activity determinations. G. S. SMITH

2373. **Determination of bismuth as bismuth phosphate by precipitation from homogeneous solution.** H. H. Ross and R. B. Hahn (Wayne State Univ., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1690–1692.—The method is based on the pptn. of bismuth phosphate with H_2PO_4 formed by the hydrolysis, in acid soln., of HPO_2 (**I**). A soln. of **I** is prepared daily (20 g in 200 ml of H_2O with 2 ml of conc. HNO_3) and filtered before use. Double pptn. removes interference by Cd, Pb, SO_4^{2-} and Cl^-. From 1 to 250 mg of Bi can be determined. The phosphate ppt. is easy to handle. The test soln. must be $\gtrsim$ 0·65N in HNO_3. *Procedure*—To a sample of alloy containing 100 to 200 mg of Bi add conc. HNO_3 (15 to 20 ml), warm, and digest for $\simeq$ 15 min. Dilute with an equal vol. of H_2O and filter off any metastannic acid. Wash the ppt. with M-HNO_3 (5 × 5 ml) and combine the washings with the filtrate. To the soln. add aq. NH_3 (1:1) until the turbidity is permanent; then add conc. HNO_3 ($\lesssim$ 10 ml) to clarify the soln. Add **I** soln. (25 ml) and dilute to 300 ml. Heat at the b.p. for 1 hr., then cool and decant the supernatant liquor through a filter-paper (Whatman No. 40). Reserve the paper after washing it with 10% NH_4NO_3 soln. (100 ml). Dissolve the ppt. in conc. HNO_3 (10 ml), add **I** soln. (25 ml), and dilute to 300 ml with boiling H_2O. Digest and cool as before. Transfer the ppt. to the reserved paper, and wash as before. Burn off the paper and ignite at red heat. Weigh the ppt. as $BiPO_4$. The method is applied to various alloys. Results agree well with those obtained by standard methods. H. A. FONER

2374. **Analytical applications of xylenol orange. V. A spectrophotometric study of the bismuth - xylenol orange complex.** K. L. Cheng (R.C.A. Laboratories, Princeton, N.J., U.S.A.). *Talanta*, 1960, **5** (3–4), 254–259 (in English).—A red complex is obtained in 0·08N to 0·15N-H_2SO_4 soln. with a maximum absorption at 540 to 545 mμ. Interference from Nb, Sb^{III} and Sn^{II} can be prevented by adding citric acid, from Mo^{VI} by adding H_2O_2, and from Fe^{III} by adding ascorbic acid. Chloride completely masks the formation of the complex. The coloured complexes of, *e.g.*, Zr, Hf, Fe and Sn, with xylenol orange are not masked in this way, so that Bi can be determined in the presence of these elements by measuring the change in extinction of the sample soln. caused by the addition of Cl^-. W. T. CARTER

2375. **Analysis of bismuth telluride and related thermoelectric materials.** H. J. Cluley and P. M. C. Proffitt (Res. Lab., General Electric Co. Ltd., Wembley, England). *Analyst*, 1960, **85**, 815–822.—To determine Bi, the finely ground sample (0·1 to 0·11 g) is dissolved in dil. HNO_3 under specified conditions, a vol. of 0·1M-EDTA (disodium salt) (standardised against pure Bi) within $\simeq$ 2 ml of the expected titre is added, and after dilution the titration is completed with xylenol orange as indicator. To determine Te in the absence of Sb, the sample ($\equiv$ 100 to 120 mg of Te) is dissolved in dil. HNO_3, urea is added to remove NO_2^-, and then dil. H_2SO_4 and 50 ml of standard $K_2Cr_2O_7$ soln. (1 ml $\equiv$ 3 mg of Te). After 30 to 45 min., $(NH_4)_2SO_4.FeSO_4$ soln., H_3PO_4 and Ba diphenylaminesulphonate indicator are added and the mixture is titrated with the $K_2Cr_2O_7$ soln., the determined equiv. of the Fe^{2+} soln. being deducted from the titre. If Sb is present, the residue from evaporation of the soln. of the sample in dil. HNO_3 is warmed with HCl, the HCl is removed by evaporation, the residue is dissolved in dil. HCl, tartaric acid soln. is added and the Te is pptd. by reduction with SO_2 and hydrazine sulphate. The collected ppt. is dissolved in dil. HNO_3 and the procedure is then as in the absence of Sb. To determine iodine, the sample is steam-distilled while dissolving in HNO_3, the distilled iodine is oxidised to iodate with Br and, after removal of excess of Br, KI is added and the liberated iodine is titrated with $Na_2S_2O_3$. A. O. JONES

2376. **Spectrophotometric determination of parts per million of iron in bismuth.** G. Signorelli (Ist. di Metallurgia, Univ. Rome). *Ann. Chim., Roma*, 1960, **50** (8–9), 1057–1060.—The sample of bismuth

in HCl soln. is treated with KSCN and the Fe-thiocyanate complex is extracted with isobutyl alcohol. The Fe is determined spectrophotometrically from the absorption maximum at 492 mμ. L. A. O'NEILL

2377. **Colorimetric and photometric determination of small amounts of vanadium.** V. G. Brudz', I. G. Shafran, K. A. Smirnova, D. A. Drapkina, S. L. Zelichenok, B. L. Podol'skaya, V. I. Maslennikova, L. K. Kuznetsova and E. M. Kazanskaya. USSR Pat. 130,703 (5.8.1960).—The reagent is di-[3-(5-amino-4-hydroxy-2,7-disulpho-2-naphthylazo)-4-hydroxyphenyl] sulphone (sulphonazo) (**I**). To determine V in aq. soln. free from interfering elements, to 2 ml of soln. (0·00005 to 0·005 mg of V) in a colourless glass tube add 2·75 ml of acetate buffer soln. [0·2N-acetic acid - 0·2N-Na acetate (1·7 : 1)] and 0·25 ml of 0·02% **I** soln. Place the tube in boiling water for 5 min., set aside for 10 min., immerse for 5 min. in water at room temp., and compare the colour of the soln. with that of standards, or measure the extinction at 620 mμ. In the presence of Al, Fe or Cu, before adding the buffer soln. add 0·5 ml of 5% NaF soln. and 0·5 ml of 10% thiourea soln. Detailed procedures are also given for determining V in a mixture containing 0·00005 g of V, 0·03 g of Mg, 0·06 g of SiO_2, 0·007 g of Fe, 0·00008 g of Ni and 0·000008 g of Ca, and for determining 10^{-2} % of V in calcium oxide. C. D. KOPKIN

2378. **Determination of vanadium in rocks and meteorites by neutron-activation analysis.** D. M. Kemp and A. A. Smales (A.E.R.E., Harwell, Berks., England). *Anal. Chim. Acta*, 1960, **23** (5), 397–410 (in English).—The method is used for the determination of V in concn. down to 0·1 p.p.m. The V is separated from the irradiated material by extraction of its cupferron complex with $CHCl_3$, and the activity is determined by liquid counting. Molybdenum and Tc interfere when the V content is relatively low. In such circumstances the Mo is removed by ether extraction of its chloride, and interference from Tc is dealt with by resolution of the composite decay curves. The extent of conflicting nuclear reactions is investigated. H. N. S.

2379. **Analysis of vanadium catalysts.** Z. Řezáč and J. Dvořák (Res. Inst. Inorg. Chem., Ústí nad Labem, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (11), 576–579.—In the presence of thioglycollic acid (**I**), V is masked and Al can be pptd. with aq. NH_3 in its presence. Iron can be determined colorimetrically with **I**. *Procedure*—Moisten the sample (1 g) in a platinum dish with H_2SO_4 (1 : 1) (2 ml), add HF (20 ml) and evaporate to fumes. Add HF (20 ml) and a few drops of HCl (1 : 1) and dilute to 250 ml. *For Fe*—Dilute 25 ml of this soln. to 250 ml with H_2O and to 25 ml add **I** (80%) (1 ml) and after 5 min. conc. aq. NH_3 (3 ml). Measure the extinction with filter S50. *For Al*—To 100 ml of the sample soln. add **I** (1 ml) and precipitate Al with aq. NH_3 by the Mayr and Gebauer method (*Z. anal. Chem.*, 1938, **113**, 189). Titanium, if present, is determined photometrically with H_2O_2 after fusing the Al_2O_3 residue with $K_2S_2O_7$. Calcium in the sample is determined flame-photometrically after separation by ion exchange, or by titration with $KMnO_4$ after pptn. as oxalate from a slightly acid medium. Sodium and K are determined flame-photometrically. J. ZÝKA

2380. **Detection of traces of oxygen in gases. The methylene blue method.** P. S. Davis (Australian Atomic Energy Comm., Lucas Heights, N.S.W.). *Metallurgia, Manchr*, 1960, **62**, 49–50.—This simple method is based upon the colour change occurring when leuco-methylene blue is oxidised. The apparatus is illustrated and described; the lower limit of detection is 100 p.p.m. (v/v) of O. J. W. O. PYEMONT

2381. **Determination of small quantities of oxygen adsorbed on anatase.** F. Cuttitta (U.S. Geol. Surv., Washington, D.C.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 488–490.—Two methods were used to determine the O (≃ 0·40%) adsorbed on to the surface of powdered anatase from the gas used in magnetic susceptibility measurements. In one method the O was desorbed at 925° and swept out with O-free N. In the second method the adsorbed O was extracted by passing a current of O-free N at room temp. over the sample. In each method the O content of the nitrogen was measured by the reaction of O with copper moistened with aq. NH_3 - NH_4Cl soln.; colorimetric measurement of the blue complex formed permits the determination of 0·1 to 2 ml of O. Full details are given of the construction and operation of the apparatus. R. A. HOWIE

2382. **Determination of oxygen in some minerals using pyrites.** Iwaji Iwasaki, Takashi Katsura and Minoru Yoshida (Technol. Inst., Ookayama Meguro-ku, Tokyo). *Bull. Chem. Soc. Japan*, 1960, **33** (10), 1340–1345 (in English).—A mixture of iron pyrites and an oxygen-containing mineral is heated *in vacuo* and the evolved gases (consisting of SO_2, H_2S and H_2O) are measured and analysed. From the results the oxygen content of the mineral may be calculated. The temp. of reaction varies with the nature of the mineral, so that by heating at successively higher temp. it is possible to determine $FeSO_4$, $Fe_2(SO_4)_3$, and Fe_3O_4. Results for such a mixture (50 mg of each) were within ± 10% of the amounts added. For pyrites alone, results for O content, on 2- and 3-g samples, were 0·067% and 0·073%, respectively. (*Cf.* Babko *et al.*, *Anal. Abstr.*, 1956, **3**, 3611; 1957, **4**, 2959.) T. R. ANDREW

2383. **The geochemistry of sulphur.** W. Ricke (Zentrallab. für Geochem. der Isotope, Göttingen, Germany). *Geochim. et Cosmoch. Acta*, 1960, **21** (1–2), 35–80.—Two chemical methods are described for the determination of small quantities of total S and sulphide S in silicate minerals and rocks. Following fusion of the finely ground sample with Na_2O_2 at 650° and oxidation of the total S to sulphate, the sulphate is separated from interfering ions and determined in methanol soln. by photometric titration with $BaCl_2.2H_2O$ soln. at 436 mμ. Sulphide S is determined by treating the sample with HCl in a current of hydrogen, the S being converted into H_2S. The H_2S is absorbed in Cd acetate soln., and treated with standard iodine soln., the excess of which is determined by titration with $Na_2S_2O_3$ soln. R. A. HOWIE

2384. **Modified sulphite method for the determination of sulphur in ores, concentrates and flotation wastes.** T. Tyniec (Sulphur Mines and Works, Tarnobrzeg, Poland). *Chem. Anal., Warsaw*, 1960, **5** (5), 775–780.—The method is based on the reaction—$S + Na_2SO_3 = Na_2S_2O_3$. *Procedure*—Add 0·2 to 0·25 g of powdered sample to a conical flask

containing ethanol (5 ml) and 15% Na_2SO_3 soln. (20 ml). Boil gently for 15 min., cool to 20°, add 36% formaldehyde soln. (5 ml), 20% aq. acetic acid (20 ml) and starch soln. (2 ml) and titrate with 0·1N-iodine. This method is much quicker (25 to 30 min.) and simpler, but not less accurate, than the classical one. B. K.

2385. **Determination of sulphuric acid in the presence of inorganic and organic acids by potentiometric titration in methanol.** W. Stuck (Anal. Lab., Farbenfabriken Bayer A.-G., Werk Uerdingen, Germany). *Z. anal. Chem.*, 1960, **177** (5), 338–344 (in German).—By titrating a mixture of H_2SO_4 and HCl in methanol with cyclohexylamine, a potentiometric curve is obtained in which the first inflection represents the neutralisation of HCl and the first equivalent of H_2SO_4, and the second inflection represents the neutralisation of the second equivalent of H_2SO_4. Results for the analysis of mixtures of H_2SO_4 with toluene-*p*-sulphonic acid, HNO_3, HCl, H_3PO_4 and $HClO_4$, respectively, are tabulated and discussed. Aq. soln. of sulphate and sulphonate mixtures are passed through a column of Wofatit KS resin, and eluted with methanol, and the acids are titrated by the method described. Sulphates of inorg. and org. bases that are soluble in methanol can be directly titrated potentiometrically with $HClO_4$. Results are tabulated. B. B. Bauminger

2386. **Application of the induced sodium azide - iodine reaction in quantitative analysis. I. Determination of traces of sulphide.** Z. Kurzawa (Dept. Gen. Chem., Politech., Poznań, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 551–565.—The effects of the following factors were established, *viz*, concentration of reactants, time, temp., pH value, stirring, reversibility and interfering ions. It was found that high initial concn. of S^{2-} and NaN_3, at least a 30% excess of iodine over S^{2-} and rapid stirring are essential. The reaction is almost instantaneous at a pH between 4·7 and 7·8. Interfering Pb^{2+}, Fe^{3+} and Cu^{2+} are masked with tartrate; a correction can be applied for Fe^{3+}, Sn^{2+}, Hg^{2+} and other ions that react with iodine. Compounds containing bivalent S interfere. *Procedure*—To 80 ml of sample (0·00025 to 0·15 mg of S^{2-}) at pH 6 to 7 add 10 ml of 20% NaN_3 soln. and 5 to 7 ml of 0·1N-HCl and make up to 100 ml ± 2 ml. Stir vigorously without splashing, add 10 ml of 0·02N-iodine and after a few seconds back-titrate with arsenite soln., with starch as indicator, or by a null-point method. Correct for iodimetric interferences by a separate titration and read the amount of S^{2-} from a calibration graph. The method has been successfully applied to the determination of S^{2-} in effluents. The accuracy is ± 2·5%.

II. Determination of traces of thiosulphates. Z. Kurzawa. *Ibid.*, 1960, **5** (4), 567–574.—Thiosulphates behave similarly to sulphides, except that the induction rate is approx. 30% lower, and the required pH range is 5 to 7. The procedure is as described above, but the useful range is wider (from 0·002 to 300 mg of $S_2O_3^{2-}$). The method should be useful for the determination of $S_2O_3^{2-}$ in effluents and in sulphites. Mixtures of S^{2-} and $S_2O_3^{2-}$ cannot be separated, and approximate figures only are obtained. P. Brych

2387. **Rapid method for the determination of sulphide, polysulphide and thiosulphate in the presence of each other.** L. Szekeres (Chem. Inst. Landwirtsch. Univ., Budapest, Hungary). *Z. anal. Chem.*, 1960, **178** (2), 81–84 (in German).—Sources of error in current methods for the determination of ionic S in alkali sulphide soln. are discussed, and the more satisfactory ones described. *Procedure*—Take 4 equal aliquots (10 to 15 ml) of test soln. and treat them as follows. (*a*) Dilute with 30 to 40 ml of H_2O, add 25 ml of 0·1N-iodine (in 6% acetic acid soln. containing KI) and titrate with 0·1N-$Na_2S_2O_3$ (*A* ml). (*b*) Add 0·1N-$KBrO_3$ (100 ml), KBr (3 g) and conc. HCl (5 ml). After dissolution of S, add 2 g of KI and titrate as described above (*B* ml). (*c*) Dissolve H_3BO_3 (2 g) in H_2O (70 ml) and de-aerate by boiling. Add 10% KCN soln. (2 ml) and then the test soln. Boil for 10 min., cool, add 10 to 15 ml of 0·1N-iodine (in acetic acid soln.) and titrate as described above (*C* ml). (*d*) Dissolve 2 g of H_3BO_3 in 70 ml of H_2O as before and add to the fourth aliquot. Boil to expel H_2S, add KBr (3 g), 0·1N-$KBrO_3$ (75 ml) and conc. HCl (10 ml). Proceed as for (*b*) (*D* ml). Then $S^{2-} = (16A + B - 16C - D)/40$; $S_2O_3^{2-} = (4A - B + 16C + D)/20$; and polysulphide $= (-24A + 6B - 16C - D)/30$. Results are given for 15 mixtures, the total sulphur contents of which (as $BaSO_4$) range from 0·15 to 0·31 g per 10 ml.
P. D. Parr-Richard

2388. **Oxidation of polythionates with chloramine T.** K. Sharada and A. R. Vasudeva Murthy (Dept. of Inorg. and Phys. Chem., Indian Inst. of Sci., Bangalore). *Z. anal. Chem.*, 1960, **177** (6), 401–403 (in English).—The S–S link in polythionates is broken by oxidation with chloramine T (**I**) and S is converted into H_2SO_4. Results are quant. *Procedure*—Add the aq. soln. to 25 ml of 0·1N-**I** acidified with 2N-acetic acid (10 ml). After a few minutes, add excess of KI and titrate with $Na_2S_2O_3$ soln. To oxidise hepta- or octa-thionates, heat the soln. at 45° to 50° with **I**.
P. D. Parr-Richard

2389. **Radiochemical determination of polythionates.** N. H. Schöön (Chalmers Tekniska Högskola, Göteborg, Sweden). *Acta Chem. Scand.*, 1960, **14** (9), 2009–2020 (in English).—Two methods have been developed for the determination of polythionates in spent liquors from the sulphite cellulose process, to which the iodimetric method (after conversion of polythionate to thiosulphate) is inapplicable. (*i*) *The AgSCN method*—The sample is treated with sulphite in the cold (to form trithionate and thiosulphate) and also with a mixture of sulphite and sulphide at 100° (to form only thiosulphate), and the amount of thiosulphate formed in both reactions is determined by the addition of AgSCN containing ^{110}Ag so that a soluble ^{110}Ag complex is formed with $S_2O_3^{2-}$ and can be determined by measuring the activity of the soln. after removal of the solid phase. Before addition of AgSCN, the excess of S^{2-} is removed as ZnS, and the excess of SO_3^{2-} is converted into HSO_3^-, to prevent the formation of soluble complexes of Ag with SO_3^{2-}. The original $S_2O_3^{2-}$ concn. of the sample is also determined, and from these figures the amount of polythionate is calculated and also the mean number of S atoms per molecule. (*ii*) *The sulphide method*—The sample is treated with SO_3^{2-} as in method (*i*), to form $S_2O_3^{2-}$ and $S_2O_6^{2-}$, and is then heated with an excess of sulphide containing ^{35}S, so that each mole of $S_2O_6^{2-}$ forms one mole of radioactive $S_2O_3^{2-}$. The excess of S^{2-} is removed as ZnS, and the $S_2O_3^{2-}$ and SO_3^{2-} in the filtrate are oxidised to SO_4^{2-}

and pptd. as $BaSO_4$, the activity of which is measured in a proportional counter of the "flow-counter" type. Method (*i*) is more sensitive to low concn. of polythionate and, when the sample contains only trithionate, the error is 3%, but rises to 9% when a higher thionate is present, and can be as much as 33% when thiosulphate is present in tenfold concentration. Method (*ii*) is more accurate, especially in the presence of thiosulphate.

C. S. Howes

2390. **Determination of micro concentrations of gold in high-purity selenium.** V. I. Shamaev and O. F. Saunkin. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 66–68; *Ref. Zhur., Khim.*, 1960, (19), No. 77,024.—*Procedure*—Irradiate the sample (0·5 g) and the standard in a reactor with a flux of $8·7 \times 10^{12}$ neutrons per sq. cm per sec. for 35 to 40 hr., wash it with hot dil. HCl and dissolve it in aqua regia. Add $HAuCl_4$ ($\simeq$ 20 mg of Au) to the soln., evaporate twice with HCl, dilute with H_2O (to 50 ml), add urea (0·5 g), boil, adjust the pH to $\simeq$ 5 with 5% NaOH soln. and precipitate Au with H_2O_2 soln. Boil the ppt. with dil. HNO_3, dissolve the residue in aqua regia, evaporate twice with HCl, dissolve the residue in 7% HCl (10 ml) and extract Au with ethyl ether. Distil off the ether. To the aq. phase add conc. HCl (1 ml) and $NaNO_2$ (50 mg) and precipitate Au by the addition of NaOH soln. Ignite the residue at 900° and determine the chemical yield. Measure the activity of the ^{197}Au. The sensitivity of the method is $\simeq 10^{-11}$ g of Au; the error in determining 10^{-6} to 10^{-9} g is 10 to 20%.

K. R. Cook

2391. **Spectrophotometric determination of selenium in the presence of tellurium.** N. Leontovitch (Inst. de Rech. de la Sidérurgie, Saint-Germain-en-Laye, France). *Chim. Anal.*, 1960, **42** (11), 549–551.—It is shown that the previously published procedure for the photometric determination of Se (*cf. Anal. Abstr.*, 1959, **6**, 4781) may be used in the presence of Te, provided that the ratio of Te to Se is at least 0·135. Under the stated conditions there is an enhancement of sensitivity in the determination of Se, which effect is shown to be due to the formation of $TeSe_{12}$. G. P. Mitchell

2392. **Photometric determination of tellurium with Bismuthiol II.** J. Jankovský and O. Kšír (Inst. for Ore Res., Prague, Czechoslovakia). *Talanta*, 1960, **5** (3–4), 238–249 (in English).—Tellurium gives a yellow benzene-soluble complex with Bismuthiol II (5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione) at pH 4·15 in the presence of EDTA. The extinction is measured at 415 mμ. Selenium is also extracted as a yellow complex under these conditions (a 10-fold excess of Se over Te gives a relative error of + 2%), and ions such as Au^{3+}, Pt^{4+}, V^{5+} and NO_3^- oxidise the reagent to a yellow benzene-soluble product. Silver, Au^{III}, Hg^{II}, Os^{VIII}, Pd^{II}, Pt^{II} and Tl^{I} interfere by pptg. the reagent, and F^-, tartrate, citrate and dithionite give low results. Sulphide ores containing > 0·01% of Te may be dissolved in conc. H_2SO_4 and analysed directly if excessive amounts of interfering ions are absent. Samples containing < 0·01% of Te are analysed by pptg. the Te and added Se carrier with $SnCl_2$. Results agree closely with those of the iodide method (*cf.* Johnson and Kwan, *Anal. Chem.*, 1951, **23**, 651).

W. T. Carter

2393. **Ferrimetric determination of uranium(IV) using Rhodamine 6G as fluorescent indicator.** Seetaramaraju Sagi and G. Gopala Rao (Chem. Dept., Andhra Univ., Waltair, India). *Talanta*, 1960, **5** (3–4), 154–161 (in English).—Quadrivalent U is titrated with 0·05N-$(NH_4)_2SO_4.Fe_2(SO_4)_3$ in 2N to 3N-HCl soln. at 98°, with 0·05% Rhodamine 6G (C.I. Basic Red 1) soln. as a fluorescent indicator. The quenching of the fluorescence at the end-point is observed in a specially constructed u.v. illumination chamber. Sexavalent U is converted into U^{IV} before titration by passage through a Jones reductor, followed by air-blowing to re-oxidise any U^{III} which is formed. For amounts of $\simeq$ 1 millimole of U the error is < 0·5%. Zinc (up to 1 g) and Cr (up to 0·04 g) do not interfere, but V and Mo, which are reduced in the Jones reductor to forms oxidisable by Fe^{III}, must be absent.

W. T. Carter

2394. **Potentiometric titrations of milligram amounts of uranium with vanadate.** T. S. Urbański (Dept. Chem. Technol., Inst. Nucl. Res., Warsaw, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 687–689.—The addition of H_3PO_4 accelerates the reaction, equilibrium being attained after about 30 sec. instead of several minutes. The results are reproducible and accurate, and the method takes no more time than do visual end-point methods; blank tests and high acidity of solutions are not necessary.

P. Brych

2395. **Rapid photometric determination of uranium with arsenazo II.** V. I. Kuznetsov and S. B. Savvin. *Radiokhimiya*, 1959, **1** (5), 589–595; *Ref. Zhur., Khim.*, 1960, (8), Abstr. No. 30,488.—Arsenazo II [3,3′-di-(1,8-dihydroxy-3,6-disulpho-2-naphthylazo)biphenyl-4,4′-diarsonic acid] (**I**) reacts similarly to arsenazo I in acid medium with Zr, Hf, Ti, Th, U^{IV} and Fe^{III}, and in weakly acid medium with Al, In, Ga, U^{VI}, Cu and Be. The complexes with **I** are more stable than those with arsenazo I; phosphates, fluorides and sulphates interfere to a less extent, and U^{VI} can be determined in soln. containing 5 to 6 mg of phosphate (as P) per ml. (86 references.)

C. D. Kopkin

2396. **A gamma-ray absorption method for the determination of uranium in ores.** A. F. Hoyte (U.S. Geol. Surv., Washington, D.C.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 504–507.—The 93-KeV γ-ray peak from ^{234}Th, the 24·1-day daughter of ^{238}U, is used to determine U in ore samples. The scintillation detector used is a NaI(Tl) crystal, optically coupled to a photomultiplier operated at 1200 V. Details are given of the pulse-height analyser used. Lead was chosen as the radiation absorber because of its *K*-absorption edge at 88 KeV, which greatly attenuates the 93-KeV peak of ^{234}Th. Good results are obtained with samples having a U content of < 0·30%.

R. A. Howie

2397. **Ion counting and accumulation system for mass spectrometry of very small samples. Application to uranium and plutonium.** G. W. Barton, jun., L. E. Gibson and L. F. Tolman (Lawrence Radiation Lab., Univ. of Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1599–1601.—The system described can be used for analysing about 2 samples per hour at the level of 2×10^{-8} to 2×10^{-7} g. Compounds

and elements other than uranium and plutonium can be determined if they are capable of maintaining an ion beam of 10^{-10} to 10^{-12} amp. for several minutes. Individual ion pulses are accumulated in a modified 256-channel pulse analyser as described. The values stored in the analyser at the end of the run are printed out in decimal form on a five line per sec. printer. Only simple corrections need be applied. E. G. CUMMINS

2398. **New methods for the determination of free acid in the presence of large amounts of uranyl salt.** S. Ahrland (Eurochemic, Mol-Donk, Belgium). *Acta Chem. Scand.*, 1960, **14** (9), 2035–2045 (in English).—Methods that have been proposed for this determination (which is complicated by the hydrolysis of UO_2^{2+}) are reviewed. The measurement of pH in salt media, acid enough to prevent hydrolysis, is theoretically the least objectionable method, but is lengthy and unsuitable for very small samples. Methods involving pptn. of U^{VI} followed by titration with alkali are subject to occlusion errors. Removal of U^{VI} on a cation-exchange column satd. with H^+, and subsequent titration of the original acid and that equivalent to the original concn. of U requires an accurate knowledge of this concn., and is unsuitable when this is high. Hydrolysis of UO_2^{2+} can also be suppressed by complex formation; oxalates and fluorides have been widely used but are not very suitable. Complexing with sulphate has now been investigated, and two methods are described. (*i*) *Determination by potentiometric titration*—The sample (0·2 ml) was added to 15 ml of satd. $(NH_4)_2SO_4$ soln., and titrated with NaOH soln., the NaOH concn. being chosen so as to give a titre of 1 to 3 ml. For samples containing up to 400 g of U per litre, this method was satisfactory (deviations $\pm$ 4%) for acid concn. down to 0·3M and, for samples containing up to 200 g of U per litre, down to 0·2M. (*ii*) *Determination by pH measurement*—The acid concn. of the sample was calculated from the change in pH (determined with a glass electrode) observed on the addition of a known volume of sample (*e.g.*, 0·2 ml) to 15 ml of satd. $(NH_4)_2SO_4$ soln. and a small volume of standard HNO_3 (*e.g.*, 1·0 ml of 0·02M). Errors were 5 to 7% for 0·25M free acid in samples containing up to 100 g of U per litre, increasing to $\simeq$ 20% for 0·025M acid. With higher concn. of U, the error increased, especially for the lower concn. of acid. C. S. HOWES

2399. **Spectrographic determination of high concentrations of vanadium, niobium and zirconium in uranium alloys.** I. Delespaul and F. Lievens (Centre d'Études Nucleaire, Mol, Belgium). *Spectrochim. Acta*, 1960, **16** (11–12), 1486–1488 (in French).—Good results have been obtained by direct sparking of metallic samples of binary uranium alloys containing V, Nb or Zr in the concn. range 0·5 to 20%. A Hilger medium spectrograph was used at 3110·7A for V, 3094·2 and 3225·5 A for Nb, 3214·2 A for Zr, and 3119·3 and 3224·3 A for U. A standard deviation of 4·5% was attained. E. G. CUMMINS

2400. **Effect of temperature on the extraction of uranyl, plutonium, ruthenium and zirconium nitrates with tributyl phosphate.** V. B. Shevchenko and I. A. Fedorov. *Radiokhimiya*, 1960, **2** (1), 6–12; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 76,966.—The extraction is made from a mixture of high-boiling hydrocarbons. It is established that the extraction of HNO_3 by tributyl phosphate (**I**) is reduced by an increase in temp.; the temp. gradient with HNO_3 of concn. $>$ 3N is not significant. The partition coeff. of $UO_2(NO_3)_2$ decreases with an increase in temp. The reaction—

$$UO_2(NO_3)_2 + 2\mathbf{I} \leftrightharpoons UO_2(NO_3)_2.2\mathbf{I}$$

is exothermic and complies with the Van't Hoff equation. As the saturation point of **I** with uranium is reached, the effect of temp. on the extraction decreases. The partition coeff. of Pu^{4+} alone and in the presence of $UO_2(NO_3)_2$ is increased by raising the temp. from 10° to 40°; after that it falls abruptly. With the acidity of the aq. phase at $<$ 0·5N with respect to HNO_3, the extraction of Pu^{4+} increases with an increase in temp. The extractability of Zr in the range 10° to 30° diminishes with rise in temp., but if the temp. is raised to $>$ 30° it increases. The minimum partition coeff. for Zr occurs between 25° and 30°. If the temp. is increased from 10° to 80°, the extractability of Ru is improved. K. R. COOK

2401. **Separation of uranium and rare-earth elements.** D. Purushottam (Andhra Univ., Waltair, India). *Current Sci.*, 1960, **29** (8), 308–309.—The aq. soln. of mixed nitrates (100 ml) is passed at a rate of 3 ml per min. through a column of Amberlite IR-120 (10 cm $\times$ 1 sq. cm) that has been treated with 100 ml of 2% NaCl soln., 300 ml of water, 200 ml of 5% HCl soln. and 300 ml of water. On elution with N-HCl, all the U is recovered in the first 350 ml of eluate. The rare-earth elements are then eluted with 1·68N-HCl (600 ml). If the ratio of rare-earth elements to U is as high as 12:1, some break-through of rare-earth elements occurs, but this can be avoided by eluting the U with 0·5N-HCl ($\simeq$ 2 litres). The complete elution of rare-earth elements then requires 1·2 litres of 1·68N-HCl. R. E. E.

2402. **Determination of radioactive zirconium in fissioned plutonium.** J. W. T. Meadows and G. M. Matlack (Univ. of California, Los Alamos Sci. Lab., N.Mex.). *Anal. Chem.*, 1960, **32** (12), 1607–1610.—The isotopes ^{95}Zr and ^{97}Zr can be determined by multiple pptn. with *p*-bromomandelic acid (**I**), which must be recrystallised from benzene before use. Tellurium is removed as the metal by pptn. with SO_2; this also reduces Pu^{IV} to Pu^{III}; Ce^{3+} are added as a holdback carrier for Am and Pu. Contamination of the ppt. by Nb is $<$ 0·3%. *Procedure*—Dissolve the sample in HCl (final concn. 6M) and add 1 ml each of Zr (5 mg per ml), Ce (10 mg per ml) and Te (10 mg per ml) carrier soln. to an aliquot. Evaporate to dryness, dissolve the residue in 3M-HCl and saturate the soln. repeatedly with SO_2, after first adjusting the vol. to 16 ml and heating to 100°. Centrifuge, reject the ppt., and add conc. HCl (10 ml). Heat to 100°, add 10 ml of **I** soln. (2·3% w/v), digest for 15 min. and dissolve the ppt. (collected by centrifuging) in aq. NH_3 (10 ml of H_2O, 6 drops of conc. aq. NH_3). Add 12M-NaOH (2 ml), dissolve the pptd. zirconium hydroxide in 8M-HCl and repeat the pptn. as before. Dissolve the ppt. in HCl (3:2), add 1 ml of Ce carrier soln. and re-precipitate with **I**. Wash the ppt., under suction, successively with 5 ml of water, ethanol and ether, dry at 110° for 15 min., and weigh as zirconium tetra-*p*-bromomandelate. The yield is $\simeq$ 75%. The β- or γ-activity is measured with conventional apparatus.

The Zr carrier soln. is calibrated gravimetrically by a single pptn. with **I**. A single determination takes 3 hr. The coeff. of variation for a single determination based on four samples with γ-counts from 60,000 to 87,000 c.p.m. per ml is 2·3%.

H. A. FONER

2403. **Determination of chlorine in chlorine dioxide.** L. N. Balashev, A. I. Kachalov and I. G. Bŷkova. USSR Pat. 131,544 (10.9.1960).—The content of ClO_2 in the sample is determined before and after reaction with $NaClO_2$, which converts Cl into ClO_2 according to the reaction $2NaClO_2 + Cl_2 = 2ClO_2 + 2NaCl$; the Cl is found by difference. The method is carried out by dividing the gas into two streams which are passed into a differential photometer or spectrophotometer, one stream being first passed through a column of $NaClO_2$. The output signal indicates the content of Cl in the original mixture.

C. D. KOPKIN

2404. **Determination of chlorine dioxide in concentrated solution in the presence of chlorine.** M. Lepeintre, J. Dupuy and J. Ouvrard (Service de Contrôle des Eaux de la Ville, Paris, France). *Chim. Anal.*, 1960, **42** (10), 498–500.—*Reagents*—(*i*) Water free from organic matter; (*ii*) dissolve tyrosine (750 mg) in M-NaOH (8 ml) and make up to 125 ml; (*iii*) dissolve Na acetate (7·45 g), ethylamine (6·2 g) and acetic acid (8 ml) in 80 ml of water, adjust the pH to 4·65 with acetic acid, and make up to 100 ml; (*iv*) dissolve Na acetate (7·45 g) in 80 ml of water, add acetic acid (10 ml) to adjust the pH to 4·45, and make up to 100 ml; (*v*) prepare a standard soln. of pure ClO_2 (*cf.* Granstrom and Lee, *J. Amer. Wat. Wks Ass.*, 1955, **27**, 177). *Procedure*—To 10 ml of (*iii*) add a suitable portion of the sample, and make up to 50 ml with (*i*) at a temp. between 0° and 4°. Shake the soln., transfer 10 ml to a 100-ml flask containing 80 ml of (*i*), 6 ml of (*ii*) and 2 ml of (*iv*) and make up to 100 ml with (*i*). Shake the mixture, and measure the extinction at 490 mμ at 1-min. intervals. Record the maximum extinction. Prepare a calibration curve under the same conditions, for concentrations of ClO_2 from 0 to 25 mg per litre.

R. M. ROWLEY

2405. **Simultaneous spectrophotometric determination of iodine and iodine chloride.** J. de Oliveira Meditsch (Escola de Engenharia, Pôrto Alegre, Brazil). *Rev. Quim. Ind., Rio de Janeiro*, 1960, **29**, 19–20.—The extinctions of a mixture of the two compounds in CCl_4 are measured at 460 and 525 mμ. The mol. extinction coeff. at these wavelengths are, for ICl, 84 and 38, and, for iodine 174 and 566. The concn. are calculated in the usual way from simultaneous equations.

L. A. O'NEILL

2406. **Note on the titration of iodide by the Andrews method.** J. J. Kipling and G. Grimes (Univ., Hull, England). *Talanta*, 1960, **5** (3–4), 278–281 (in English).—It has been confirmed experimentally that a satisfactory titration by the Andrews method (*J. Amer. Chem. Soc.*, 1903, **25**, 756) cannot be carried out in soln. $< 3N$ in HCl. The function of the Cl^- is to convert ICl into ICl_2^-, but the amount present is considerably greater than required for this reaction. It is not known whether the high concn. of H^+ and Cl^- which are present function as reactants or catalysts.

W. T. CARTER

2407. **Polarographic determination of zinc in manganese, ferromanganese and manganese ores.** M. Veselá (Res. Inst. Metals, Panenské Břežany, Czechoslovakia). *Hutn. Listy*, 1960, **15** (10), 805–806.—*Procedure*—To 1 g of finely powdered sample add, in portions, 6·5N-HCl (30 ml), and boil. Filter off the silicic acid, wash the filter with 6·5N-HCl, cool and add the filtrate to a column of Wofatit L-150 (1 ml per min.), previously washed with 6·5N-HCl. Elute Mn, Co, Fe, Ni and Cu with 1·5N-HCl (200 ml), and Zn with 0·05N-HCl (200 ml). Evaporate the eluate containing Zn to dryness on a sand bath, dissolve the residue in HCl (1:2) (5 ml), add aq. NH_3 (1:1) (19 ml), satd. Na_2SO_3 soln. (1 ml) and gelatin soln. (0·5%) (1 ml), and dilute with H_2O to 50 ml. Register the polarographic wave from $-0·8$ V. As little as 0·0002% of Zn in a 3 to 5-g sample can be determined.

J. ZÝKA

2408. **Spot test for iron by substituted violuric acids.** R. P. Singh (Dept. of Chem., Univ., Delhi). *J. Indian Chem. Soc.*, 1960, **37** (7), 442.—Place the sample soln. (1 drop) on Whatman No. 1 filter-paper or on a spot tile and add acetate buffer soln. (pH 4·5) (1 drop), a trace of quinol and a 0·5% soln. of 1,3-diphenyl-, 1,3-di-*o*-tolyl- or 1,3-di-*p*-tolyl-2-thiovioluric acid in acetone (1 drop). A deep-blue colour indicates the presence of $\leqslant 0·1$ μg (paper) or 0·05 μg (tile) of Fe. Oxalate, citrate, tartrate and cyanide ions must be absent. Most cations do not interfere in concn. < 1 in 10^5.

A. R. ROGERS

2409. **Coulometric titration of iron(II) by electrolytically generated bromine.** Takeo Takahashi and Hiroshi Sakurai (Inst. of Ind. Sci., Univ. Tokyo, Japan). *Talanta*, 1960, **5** (3–4), 205–212 (in English).—Bromine reacts more rapidly with Fe^{II} in acetic acid - Na acetate medium than it does in the presence of H_2SO_4. The most suitable electrolyte contains 0·1M-KBr, N-acetic acid and 0·2N-NaOH, and 0·01 to 0·1 milli-equiv. of Fe^{II} can be titrated with an error of $\simeq 1\%$ if the coulomb value is corrected by a factor of 0·9466. The end-point is detected potentiometrically (platinum and saturated calomel electrodes) or amperometrically. The apparatus used has been described previously (*Rep. Res. Inst. of Ind. Sci., Univ. Tokyo*, 1955, **5**, 122).

W. T. CARTER

2410. **Analytical applications of 3-acetyl-4-hydroxycoumarin. II. Spectrophotometric determination of iron(II).** A. N. Bhat and B. D. Jain (Dept. of Chem., Univ. Delhi, India). *Talanta*, 1960, **5** (3–4), 271–275 (in English).—The reagent forms a red - orange complex with Fe^{2+} which is soluble in 50% ethanol. The colour of the complex is stable for several days and is independent of temp. in the range 5° to 40° and of pH in the range 2·8 to 4·3. The absorption maximum is at 400 mμ and Beer's law is obeyed from 1·5 to 5·3 p.p.m. of Fe^{II}. Bivalent Cu, molybdate, tungstate and citrate interfere seriously.

W. T. CARTER

2411. **Application of X-ray diffraction to the quantitative analysis of the oxides of iron.** M. Robert, G. Pomey and M. Angeli. *Chim. Anal.*, 1960, **42** (11), 533–542.—An X-ray diffraction technique, with Geiger - Müller counting, is used to relate the relative intensities of the diffracted lines of a crystalline substance and an internal standard to the quantitative composition of that substance. The necessary theoretical and practical requirements for the choice of the internal standard are

given, and a practical example of the analysis of iron ores for FeO, Fe_2O_3 and Fe_3O_4, with CaF_2 as internal standard, is described.

G. P. MITCHELL

2412. **Preparation of iron-ore samples for spectrographic analysis for rare elements.** B. Ya. Kaplan and L. M. Lifshits. USSR Pat. 131,540 (10.9.1960).—The Fe is distilled off from the sample as $FeCl_3$ by chlorination with NH_4Cl at 500°. The sample is mixed with a sixfold excess of NH_4Cl, the mixture is heated at 350° for 20 to 30 min. in a closed porcelain crucible, the temp. is increased to 500°, the porcelain cover is removed from the crucible and the $FeCl_3$, with the excess of NH_4Cl, is completely distilled off. Any Fe remaining on the walls of the crucible or the surface of the residue, due to hydrolysis of $FeCl_3$ and decomposition of the $Fe(OH)_3$, is removed by adding 1 to 1·5 g of NH_4Cl and again heating at 500°, if necessary repeating this treatment. The residue is analysed spectrographically.

C. D. KOPKIN

2413. **Spectrographic determination of traces of admixtures in iron.** M. Kotrbová (Phys. Inst., Acad. Sci., Prague). *Hutn. Listy*, 1960, **15** (10), 802–803.—For the determination of Mo, Sb, Sn and Bi (10^{-3} to 10^{-4} %), the sample (1 g) is dissolved in H_2SO_4 (10%) (24 ml), $CuSO_4.5H_2O$ soln. (≡ 10 mg of Cu) is added and the vol. is made up to 100 ml with 0·5N-H_2SO_4. The soln. is heated and H_2S is passed into the boiling liquid. The ppt. is filtered off, dried, ignited for 2 hr. at 450° in a porcelain crucible and examined in a Q24 spectrograph, with the use of graphite electrodes and standards.

J. ZÝKA

2414. **Micro-determination of ferrous iron in silicate minerals by a volumetric and a colorimetric method.** A. D. Wilson (D.S.I.R., Lab. of the Gov. Chemist, Geological Survey and Museum, London). *Analyst*, 1960, **85**, 823–827.—To the ground sample (3 to 20 mg) in a polystyrene vessel is added 0·1 ml of 0·139N-V^V soln. (NH_4VO_3 in 2N-H_2SO_4) from a micrometer-syringe burette, and then 1 ml of HF, and the mixture is set aside until dissolution is complete. After addition of 10N-H_2SO_4 (3 ml), and when any pptd. fluorides have re-dissolved, Ba diphenylaminesulphonate indicator and 3 ml of water are added and the liquid is titrated with 0·139N-$(NH_4)_2SO_4.FeSO_4$. A reagent blank is determined. For the colorimetric method, the sample is decomposed as in the volumetric method, then 0·1 ml of the V^{5+} soln. and 5 ml of aq. 50% (w/v) $BeSO_4.4H_2O$ soln. are added, and the mixture is added to 5 ml of 0·15% aq. 2,2′-bipyridyl and 10 ml of 50% ammonium acetate soln. diluted to ≃ 50 ml (ensuring a pH of 5). After dilution of the soln. to 100 ml, the extinction is measured at 525 mμ against water. The reagent blank is deducted and a control determination is made with silicate rock of known Fe^{3+} content. Organic carbon, pyrolusite and sulphides of Fe interfere.

A. O. JONES

2415. **Spectrophotometric method for the determination of ferrous oxide in rocks.** L. Shapiro (U.S. Geol. Surv., Washington, D.C.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 496–497.—A method is described which can be adapted to the analysis of a large batch of samples. *Procedure*—Transfer the sample (10 mg, 200 mesh) to a dry plastic bottle. Add 20 mg of powdered 1,10-phenanthroline, H_2SO_4 (1:10) (3 ml) and HF (0·5 ml) and heat on a steam bath for 30 min. Remove the bottle from the bath, add 10% Na citrate soln. (20 ml), transfer the contents to a 100-ml flask containing 5% H_3BO_3 soln. (5 ml) and make up to volume. Determine the extinction at 555 mμ in a 25-mm cell. Read the extinction also at 640 mμ against a reference blank, to give a correction for any fine ppt. formed, as with limestone.

R. A. HOWIE

2416. **Determination of the ferrous iron contents of carbonaceous shales.** G. D. Nicholls (Geol. Dept., Univ. Manchester, England). *J. Sediment. Petrol.*, 1960, **30** (4), 603–612.—A rapid method for the determination of FeO in the presence of organic matter equivalent to up to 4% of C is described. After initial attack of the sample with HF - H_2SO_4 and the addition of H_3BO_3 (2 g) the soln. is poured into a stoppered bottle containing conc. HCl (75 ml) and iodine chloride (6 ml), the latter reagent being prepared by dissolving KI (10 g) and KIO_3 (6·44 g) in HCl (1:1) (150 ml). Pure CCl_4 (10 ml) is added and the bottle is shaken for 20 sec. Standard KIO_3 soln. is added, with intermittent shaking, until the mauve colour almost disappears from the CCl_4 layer; a further 10 ml of CCl_4 is then added to form a zone free from carbonaceous material at the bottom of the bottle in which the end-point (discharge of the mauve colour) can be readily detected. The KIO_3 soln. may be standardised against the $KMnO_4$ used for determining, after reduction, the total iron content of the rock.

R. A. HOWIE

2417. **Methods for determination of some trace elements in cast iron.** R. C. Rooney (B.C.I.R.A., Alvechurch, Birmingham). *B.C.I.R.A. Journal*, 1960, **8** (5), 703–716.—The latest procedures for determination of traces of Sb, Bi, Pb, Co and acid-sol. and acid-insol. Al, in amounts down to 0·1 to 1 p.p.m., with an accuracy of ± 10%, are described. Recommendations are made with respect to apparatus, reagents and procedures, based on experience gained in their use. It is pointed out that for consistent results the highest quality reagents are necessary, which is reflected in the cost. Comparative tables of cost are given. Refinements in analytical techniques are mentioned and the interpretation of results is discussed, with a table of scatter of results for Pb, Al and Bi. Procedures are given for various ranges of concn.

C. H. COWPER-COLES

2418. **Electrolytic dissolution of stainless steel.** V. A. Mchedlishvili, G. A. Lyubimova and A. M. Samarin (A. A. Balkov Inst. of Metallurgy, Acad. Sci., USSR). *Zavod. Lab.*, 1960, **26** (11), 1212–1219.—Dissolution at a c.d. of 0·03 to 0·05 amp. per sq. cm in a flowing neutral anolyte containing 5% of KSCN, 1% of Na citrate and 0·08% of As_2O_3, with a catholyte composed of 5% Na citrate treated with citric acid to give a pH of 2·5 to 3, is recommended.

G. S. SMITH

2419. **Photometric determination of boron in steel by means of brilliant green.** A. K. Babko and P. V. Marchenko (Inst. of Gen. and Inorg. Chem., Acad. Sci., USSR). *Zavod Lab.*, 1960, **26** (11), 1202–1206.—The sample (0·5 g) is dissolved by gentle heating under reflux in 12 ml of H_2SO_4 (1:4) and the cooled liquid is treated with 0·5 to 2 ml of H_2O_2 (30%) and boiled for 30 min. The

soln. is diluted to 25 ml and an aliquot (5 ml) in a plastic or platinum vessel is treated with 2 ml of 2M-NH_4F. After 30 min., 1 or 2 drops of 0·5% brilliant green (C.I. Basic Green 1) soln. is added and the soln. is neutralised with ≃ 40% hexamine soln. A further amount (0·5 to 1 ml, depending on the expected content of B) of the brilliant green soln. is added, and the soln. is shaken with 5 ml (accurately measured) of benzene. The aq. layer, together with 0·5 to 1 ml of the benzene layer, is run off and the extinction of the remaining benzene layer is measured with a 610-mμ filter. The content is calculated by means of a calibration curve. Standardisation under identical conditions is essential, since only ≃ 60% of the boron complex is extracted. With a sample wt. of 0·1 g, 5×10^{-4}% of B can be determined. G. S. SMITH

2420. **Use of controlled atmospheres to minimise matrix effects in the spectrographic analysis of tool steel.** R. F. Majkowski and T. P. Schreiber (Res. Lab., Gen. Motors Corp., Warren, Mich., U.S.A.). *Spectrochim. Acta*, 1960, **16** (10), 1200–1208 (in English).—Methods of sample excitation which result in a black burn due to the deposition of graphite from the counter-electrode on the sample surface are shown to lead to an appreciable reduction in matrix effect. This deposition is brought about by introducing N or Ar into the analytical gap. A less pronounced reduction in matrix effect is brought about by violent burn conditions induced by introducing O into the gap. G. SKIRROW

2421. **Colorimetric - chromatographic ultramicro-analysis of gases. III. Determination of ultra-micro amounts of carbon in technical iron and iron alloys.** J. Juránek and A. Ambrová (Inst. Petroleum Res., Brno, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (11), 2814–2821 (in German).—For the determination of C in iron in the presence of S, the sample is burnt in a stream of O, the CO_2 and SO_2 are separated chromatographically on a silica-gel column (5 mm × 5 cm) and the CO_2 is passed into the photometry cell (Juránek, *Ibid.*, 1959, **24**, 135); 10^{-2} μg of C can thus be determined in a 1-g sample with an accuracy within ± 10%, and 0·001% of C in a 0·1-g sample within ± 1%. The method is suitable for routine analysis; one determination requires 25 min. J. P. STERN

2422. **Photometric determination and surface detection of silica in steel.** M. Pangrác (ČKD - Praha, Sokolovo, Czechoslovakia). *Hutn. Listy*, 1960, **15** (10), 807–808.—*Detection*—Apply HNO_3 (1:1) (1 drop) to the polished surface of the test sample, then transfer the soln. to a 25-ml flask. Dilute with H_2O (5 ml), add H_2SO_4 (1:4) (3 or 4 drops), boil, dilute with a small vol. of H_2O, add ammonium molybdate soln. (5%) (1 to 2 ml) and heat gently; after 2 min. add oxalic acid soln. (10%). Dilute to vol. with H_2O and compare the blue colour with a standard. Samples of high-alloy steels are treated with HNO_3 - HCl. *Photometric procedure*—Dissolve the sample (0·25 g) in a mixture of H_2SO_4 and HNO_3 (72 ml of conc. H_2SO_4 and 91 ml of conc. HNO_3 diluted with H_2O to 1 litre) (35 ml). Dilute with H_2O (20 ml), boil, cool and dilute with H_2O to 500 ml. To 20 ml add ammonium molybdate soln. (2·5%) (10 ml), and after exactly 10 min. oxalic acid soln. (5%) (10 ml) and $(NH_4)_2SO_4.FeSO_4$ soln. (0·6% with 4 drops of H_2SO_4 per litre) (5 ml). Dilute with H_2O to 250 ml and measure the extinction in a Pulfrich photometer, with a S66 filter. Carry out a blank and compare with a calibration curve. J. ZÝKA

2423. **Photometric determination of tin in steel.** I. Janoušek and K. Študlar (Res. and Control Inst., Z.V.I.L., Plzeň, Czechoslovakia). *Hutn. Listy*, 1960, **15** (11), 889–893.—*Procedure for* 0·001 *to* 0·1% *of Sn*: (*i*) *Separation on Anex L*—Dissolve the sample (2 g) in HCl (1:1) (30 ml) by heating, cool, oxidise dropwise with H_2O_2 (30%) (5 ml), heat gently for 3 to 5 min., cool, transfer into a 50-ml flask, dilute to vol. and filter, discarding the first portion and passing 25 ml of the remainder of the filtrate through a column of Anex L (1 ml per min.). Wash the column with 2N-HCl (2 × 5 ml and 40 ml), then elute the Sn with 0·8N-HNO_3 (98 ml). Dilute the eluate to 100 ml and transfer 15 ml to a 50-ml flask. Add $CuSO_4$ soln. (1 ml) (= 2 mg of Cu), then conc. aq. NH_3 dropwise till the soln. is blue, decolorise with 2N-HCl and add 3 ml in excess. Add thiourea soln. (10%) (1 ml) and an ethanolic soln. of quercetin (0·04%) (25 ml), dilute to vol. and measure the extinction at 420 mμ against a blank. Compare with a calibration curve. The method requires 3·5 to 4 hr. The presence of Mo and W causes interference. (*ii*) *Separation by distillation*—Dissolve the sample (2 g) as above, filter, wash with hot HCl (1:50) and dilute to 50 ml. To 5 ml add slowly conc. H_2SO_4 (20 ml) and KBr soln. (40%) (15 ml), mix and heat to 140°. Add HCl (40 ml) dropwise, maintaining the temp. between 135° and 145°. Distil until the temp. reaches 170°. To the distillate add NaCl (0·3 g) and evaporate to about 3 ml. Dilute with H_2O (10 ml), add $CuSO_4$ soln. and proceed as described above. Both methods were used for the determination of Sn in steel containing Mn, Si, P, Cr, Ni, Co and V, and the distillation method also for samples containing Mo and W. Both methods gave errors of up to ± 10 to 15% (relative). J. ZÝKA

2424. **Phase analysis of nitrided low-carbon steels containing niobium.** Yu. A. Klyachko, M. M. Shapiro and E. F. Yakovleva. *Zavod. Lab.*, 1960, **26** (11), 1219–1223.—The electrolytic separation, X-ray analysis, and chemical analysis of the nitro-carbide phase are described. G. S. SMITH

2425. **Separation and determination of the nitrides of aluminium and silicon [present in steel].** M. I. Shvalger. *Zavod. Lab.*, 1960, **26** (11), 1223–1228.—A review of published work, with 26 references, is presented. G. S. SMITH

2426. **Ion-exchange separation of titanium from steels and its determination with hydrogen peroxide.** V. T. Athavale, M. N. Nadkarni and C. Venkateswarlu (Atomic Energy Estab. Trombay, Bombay, India). *Anal. Chim. Acta*, 1960, **23** (5), 438–440 (in English).—Titanium is separated from Fe, Cr, Ni, V, Mo, Co, Mn, W, Nb and Ta by means of an anion-exchange column. The Ti is retained from a soln. in dil. HF and is eluted with 3N-HCl. *Procedure*—Dissolve the sample (0·2 g) of steel in conc. HCl (10 ml) with the addition of a few drops of conc. HNO_3, and evaporate to dryness. To the residue add conc. HCl (2 ml), transfer to a polyethylene beaker, add 40% HF (4 ml) and dilute to 200 ml. Pass the soln. through a column (6 cm × 1 cm) of Amberlite IRA-400 resin, and wash the column with a mixture of conc. HCl (2 ml),

40% HF (4 ml) and water (194 ml), or twice these quantities if V is present. Then wash the column with water (50 ml). Elute the Ti with 3N-HCl (25 ml) and wash the column with water (50 ml). To the eluate add H_2SO_4 (1:1) (10 ml) and evaporate to fuming. Dilute to 40 ml, add 30-vol. H_2O_2 (1 ml), dilute to 50 ml and determine the extinction at 425 mμ. H. N. S.

2427. **Macro- and micro-determination of traces of cobalt. VIII. Direct determination of cobalt in Inconel, by activation with thermal neutrons: limits of determination and interferences.** W. Haerdi, J. Vogel and D. Monnier (Lab. Chim. Min., Chim. Anal. et Microchim., Univ., Genève). *Helv. Chim. Acta*, 1960, **43** (6), 1585–1595 (in French).—The procedure described permits the assay of traces of Co in Inconel without dissolution or separation. The sample is irradiated with thermal neutrons and the γ-ray spectrum is recorded with a single-channel spectrometer provided with a thallium-activated NaI crystal coupled with a photomultiplier detector. Results obtained by the use of internal and external standards, and by separation, of Co, are discussed. The method is satisfactory for 0·1-mg samples, and Fe or Ni in concn. up to 60 and 200 times that of Co, respectively, do not interfere. A. G. Cooper

2428. **Spectrophotometric determination of cobalt in copper alloys.** G. Lindley (English Electric Co. Ltd., Bradford, England). *Metallurgia, Manchr*, 1960, **62**, 45–49.—A simple method is described. The effects of acidity, Cu and other elements are discussed. The sample (0·2 g) is dissolved in HNO_3 (sp. gr. 1·42). The diluted soln. is electrolysed to remove Cu. The soln. is then evaporated to dryness, the residue is dissolved in 20 ml of HCl (sp. gr. 1·175) and the extinction is measured at 625 mμ. Results are referred to a calibration curve. J. W. O. Pyemont

2429. **Determination of small amounts of cobalt in highly alloyed metals.** R. C. Rooney (B.C.I.R.A., Alvechurch, Birmingham, England). *Metallurgia, Manchr*, 1960, **62**, 175–180.—The spectrophotometric determination of Co in cast iron and steel by the use of 2-nitroso-1-naphthol (*Anal. Abstr.*, 1959, **6**, 2981) has been extended to highly alloyed steels, ferro-alloys, etc., and the behaviour of a number of elements in such a determination was investigated. The naphthol reagent, used as a 0·1% soln. buffered with acetate to pH 5, gives ppt. with Ni, Hg, Ag, Fe^{3+}, Cu^{2+} and Cr^{3+}, but all these elements, except Ni and Cr, can be removed by extraction with $CHCl_3$ and cupferron. The ppt. of Ni and Cr^{3+} are dissolved by the addition of 10N-HCl, and the Co is extracted with benzene and determined spectrophotometrically. Interference due to discoloration of the 2-nitroso-1-naphthol reagent is minimised by restricting the amount used to 10 ml per determination (≡ 30 mg of Ni). Most samples can be dissolved in aqua regia, with addition of HF for ferro-alloys. Results for a wide range of materials are given and compare satisfactorily with those from previous B.I.S.R.A. determinations. M. G. Seaman

2430. **Separation of microgram amounts of cobalt in nickel metal by tributyl phosphate.** V. T. Athavale, S. V. Gulavane and M. M. Tillu (Atomic Energy Estab. Trombay, Bombay, India). *Anal. Chim. Acta*, 1960, **23** (5), 487–490 (in English).—The method is suitable for the determination of 5 to 50 p.p.m. of Co in nickel. The sample (1 g) is dissolved in conc. HCl, the soln. is evaporated to dryness and the residue is dissolved in 20 ml of 10·5N-HCl. The Co is extracted from this soln. by shaking with four 40-ml portions of a soln. prepared as follows. Tributyl phosphate is purified by extraction with 5% Na_2CO_3 soln., and a 40% soln. of the purified material in white spirit is equilibrated by shaking with 10·5N-HCl. The combined extracts are washed with water (4 × 40 ml) and then evaporated to dryness. The organic matter is removed by repeated evaporation with HNO_3 and a few drops of H_2O_2. The dry residue is dissolved in water and the Co is determined spectrophotometrically with nitroso-R salt. A small correction is applied for the amount (10 to 12 mg) of Ni that is extracted with the Co. H. N. S.

2431. **Co-precipitation of cobalt with nickel dicyandiamidinate.** I. M. Korenman, F. R. Sheyanova and G. A. Shapkin. *Trudy Khim. i Khim. Tekhnol.*, 1959, (2), 393–396; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 76,949.—The radioactive isotope ^{60}Co is used to study the separation of nickel dicyandiamidinate from small amounts of Co. It is established that the extent of co-pptn. is dependent on the Co or Ni content in soln., the sedimentation rate, and the presence of electrolyte and protective colloids. The adsorptive nature of co-pptn. is demonstrated and the adsorption isotherm calculated. The absolute amounts of co-pptd. Co are small and they do not affect the accuracy of the Ni determination. The determination of Co in the filtrate is not accurate, since 10 to 20% of it may be adsorbed by the ppt. K. R. Cook

2432. **Use of diphenylthiovioluric acid as reagent for gravimetric estimation of metals. III. Estimation of nickel.** R. P. Singh (Chem. Dept., Univ., Delhi). *J. Sci. Ind. Res., India, B*, 1960, **19** (12), 468–469.—The ammonium salt of 1,3-diphenyl-2-thiovioluric acid is a suitable reagent for the gravimetric determination of Ni in soln., either alone or in the presence of small quantities of Cu or Fe. To a soln. (30 ml) containing 0·015 to 0·030 g of Ni and ≃ 1·5 g of NH_4Cl, adjusted to pH 4·0 to 5·8 and heated to 90°, a soln. of the reagent (≃ 8%) (200 ml) is slowly added, with constant stirring. The mixture is digested on a water bath for 30 min., then set aside for 2 hr. and the ppt. is collected in a sintered glass crucible No. 4, washed thoroughly and dried at 110°. It is weighed as NiD_2, in which D is the diphenylthioviolurate radical. Neither Cu (up to 0·1%) nor Fe^{III} (up to 0·1%) interferes if the pptn. is carried out in the presence of K tartrate at pH 4·0 to 5·0 (if Cu is present) or at pH 5·0 to 5·8 (if Fe^{III} is present). Differences between the wt. of Ni found and that calculated ranged from 0·10% to 0·25% (Ni alone, 6 determinations), 0·14% to 0·47% (in the presence of Cu, 6 determinations) and 0·05% to 0·30% (in the presence of Fe^{III}, 5 determinations); Ba, Sr, Mg and Zn cannot be determined with this reagent. I. A. Simpson

2433. **Spectrophotometric determination of microgram amounts of nickel with Solochrome red ERS.** G. E. Janauer and J. Korkisch (Anal. Inst. der Univ. Wien, Austria). *Z. anal. Chem.*, 1960, **177** (6), 407–412 (in German).—In the reaction of Ni with Solochrome red ERS (C.I. Mordant Red 7) (**I**), only Fe, Cu, Co, Al, Zr, Ti and some organic acids interfere. Copper and Fe are removed by

ion exchange, and Al, Zr and Ti are complexed with F^-. *Procedure*—Evaporate the soln. (≯ 15 μg of Ni) to dryness and ignite the residue; dissolve it in 4N-HCl and evaporate to dryness at 100°. Add 0·1N-HCl (1 ml) and H_2O (≯ 7 ml) and transfer to a 10-ml flask. Add 0·5 to 1 ml of a 0·035% aq. soln. of **I** and 0·5 ml of 2·5M-Na acetate as buffer. Dilute to 10 ml, heat for 2 min. at 100° (5 min. for blank), cool rapidly and measure the extinction at 510 mμ. The sensitivity is 1 μg of Ni per 10 ml; Beer's law is obeyed for 0 to 15 μg of Ni. P. D. PARR-RICHARD

2434. **Co-precipitation of zinc by precipitation of nickel with an ammoniacal Naphthol yellow solution.** I. M. Korenman, P. A. Ganichev and A. T. Slepneva. *Trudy Khim. i Khim. Tekhnol.*, 1959, (2), 401–405; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 76,950.—Naphthol yellow (2,4-dinitro-1-naphthol-7-sulphonic acid) in ammoniacal medium gives a yellow cryst. ppt., the form of which is suitable for microcrystalloscopic analysis. A study is made of the quant. relationship between the co-pptn. of Zn and the NH_3 concn., the reagent concn., temp. and duration of settling of the ppt., the concn. ratio of Ni to Zn, and the presence of impurities and colloids. The adsorptive nature of the co-pptn. is established. K. R. COOK

2435. **Paper-chromatographic and -ionophoretic separation of the platinum [group] elements and of gold.** E. Blasius and M. Fischer (Anorg.-Chem. Inst., Tech. Univ., Berlin). *Z. anal. Chem.*, 1960, **177** (6), 412–420 (in German).—It is possible to separate mixtures of Pt, Pd, Os, Ir, Ru, Rh and Au, although better separations were obtained for ternary mixtures of Ru, Rh and Pd, or Pt, Os and Ir. The metals were used in the form of their chloro-, nitrito- or nitrosochloro-complexes; full experimental details and specific reagents for their detection are given. P. D. PARR-RICHARD

2436. **Spectrophotometric determination of rhodium with sym.[1,5]-diphenylcarbazone.** G. H. Ayres and F. L. Johnson, jun. (Univ. of Texas, Austin, U.S.A.). *Anal. Chim. Acta*, 1960, **23** (5), 448–457 (in English).—1,5-Diphenylcarbazone soln. is oxidised by air to a 1:1 mixture of 1,5-diphenylcarbazone and 1,5-diphenylcarbazide. This yields a purple colour with Rh^{3+} and affords a spectrophotometric method for the determination of the metal in the optimum concn. range 0·3 to 1·5 p.p.m. The mechanism of the reaction is discussed. *Procedure*—Treat the sample with 10 ml of $HClO_4$ (70 to 72%), evaporate to a vol. of 1 to 2 ml, dilute with water and adjust to pH 3·0. Neutralise 0·1M-chloroacetic acid to pH 3·0 with NaOH soln., and make the soln. 0·1M with respect to $NaClO_4$. To 5 ml of this soln. add $(10 - n)$ ml of 0·1M-$HClO_4$ that has been neutralised to pH 3·0, then add an aliquot (n ml) of the sample soln. and 1 ml of a 0·025M soln. of 1,5-diphenylcarbazone in acetone containing 0·01% by vol. of acetic acid. Heat in boiling water for 30 min., cool, transfer to a 50-ml flask, rinse with methanol and 5 ml of dimethylformamide and dilute to 50 ml with methanol. Measure the extinction at 565 mμ against a reagent blank. The following metals interfere when originally present in concn. greater than that indicated (in p.p.m.)—Pd, 1·5; Pt, 10; Ir, 5; Au, 10; Fe, 9; Co, 2; Ni, 0·5; Ag, 12; Zn, 4; and Pb, 5; Cu, Cr, Hg and SO_4^{2-} must be absent. H. N. S.

2437. **The analytical chemistry of the platinum metals. IX. Gravimetric determination of iridium with phosphonium and arsonium salts.** R. Neeb (Inst. für anorg. Chem. u. Kernchem., Univ. Mainz, Germany). *Z. anal. Chem.*, 1960, **177** (6), 420–424 (in German).—Pptn. of Ir from dil. HCl soln. with benzyltriphenylphosphonium chloride (**I**) or tetraphenylarsonium chloride (**II**) is quant. within ± 1·7%. *Procedure*—Warm a soln. of Ir^{IV} (≮ 1 mg of Ir per ml) in 0·2N to 0·5N-HCl to 50° and slowly add 0·04M-**I** or **II**, with vigorous stirring, until pptn. is complete and the supernatant liquid is ≃ 0·01M in reagent. Filter after a few hours, wash with a satd. aq. soln. of the compound pptd. and dry at 110° to 130°. The conversion factors for **I** and **II** are 0·1734 and 0·1647, respectively. Other platinum metals interfere. P. D. PARR-RICHARD

2438. **Spectrophotometric determination of platinum. o-Phenylenediamine as a reagent.** J. G. Sen Gupta (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1960, **23** (5), 462–466 (in English).—*o*-Phenylenediamine (**I**) forms an orange-coloured 2:1 complex with Pt^{IV}. The reaction is applied to the determination of Pt in the optimum concn. range 4 to 12 p.p.m. *Procedure*—To the sample soln. add 5 ml of a 1% soln. of **I** containing a little acetic acid, dilute to 25 ml with an acetic acid - Na acetate buffer soln. (pH 3·42), set aside for 25 min. and measure the extinction at 450 mμ. The tolerance limits for most of the common metals lie in the range 8 to 32 p.p.m., even when the tolerance is improved by the addition of tartaric acid. H. N. S.

2439. **Infra-red techniques in the identification and measurement of minerals.** W. M. Tuddenham and R. J. P. Lyon (Kennecott Res. Center, Salt Lake City, Utah, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1630–1634.—The scope and problems of the method are reviewed. The effect of particle size on the absorption spectrum is discussed and a reproducible method of hand grinding is described. Max. reproducibility for quartz (10 mg) is attained by grinding the sample 3 separate times with 5 drops of ethanol. This method of hand grinding was satisfactory for a single mineral ground by one operator, but, with mixed minerals, operator-variation was encountered, and an automatic grinding technique was adopted. In certain circumstances the samples (in the potassium bromide discs used) conform to Beer's law. The method is applied to the measurement of the quartz in industrial dusts, the determination of the CO_2 content of carbonate-apatite rocks, and the correlation of Li content with curve shape in a series of lepidolite micas. The potassium bromide disc method is thought to be the best technique for the i.r. study of most minerals. (16 references.) H. A. FONER

2440. **Rapid method for the determination of the principal elements in natural silicate rocks. I.** A. Behr, M. L. Blanchet and L. Malaprade (Centre de Rech. Pétrograph. et Géochim., Univ. Nancy, France). *Chim. Anal.*, 1960, **42** (10), 501–507.—The scheme given is designed so that an experienced chemist can complete eight analyses in six working days. Full directions are given for the following determinations—(*i*) loss of weight at 1000° (on 1 g); (*ii*) fusion with NaOH and colorimetric determination of SiO_2 as the molybdosilicate complex at 650 mμ, and of Al_2O_3 as the Al - Ca - Alizarin S complex at 475 mμ (on 50 mg); (*iii*)

dissolution in HF - H_2SO_4 and determination of FeO by titration with $K_2Cr_2O_7$ (on 0·5 g); and (*iv*) dissolution in HF - H_2SO_4 and determination of the following elements (on 2 g). Total Fe (as Fe_2O_3) is determined by reduction with $TiCl_3$ in the presence of tungstoarsenate and titration with $K_2Cr_2O_7$; MnO by oxidation with KIO_4 and colorimetric measurement of the $KMnO_4$ at 525 mμ; TiO_2 by the extinction at 425 mμ of the yellow complex formed with H_2O_2; CaO and MgO by titration with EDTA; P_2O_5 by the extinction of molybdovanadophosphoric acid at 430 mμ; and Na_2O and K_2O by flame photometry. The results are tabulated of a series of determinations carried out by three workers on granite and basalt over a period of several months.

II. A. Behr, M. L. Blanchet and L. Malaprade. *Ibid.*, 1960, **42** (11), 557–561.—Modifications to published methods of rapid analysis for Si, Al, Fe, Ca and Mg in silicate rocks are given, and experiments are described for determining the effects of these modifications on accuracy. The reduction of the blue molybdosilicate complex with ascorbic acid is favoured for the determination of Si. The effect of Ti on the colorimetric Alizarin S method for Al, the volumetric determination of Fe by reduction of Fe^{3+} with $TiCl_3$ in the presence of arsenotungstic acid, and the determination of Ca and Mg in the presence of Fe, Al, Ti and P by the use of "blocking" agents are discussed and investigated by the use of synthetic granites.

R. M. Rowley
G. P. Mitchell

2441. **Mineralogical analysis of carbonate rocks by X-ray diffraction.** P. W. Hughes, W. F. Bradley and H. D. Glass (Illinois State Geol. Surv., Urbana, U.S.A.). *J. Sediment. Petrol.*, 1960, **30** (4), 619–626.—A procedure is described for the identification of minerals present in amounts $> 5\%$ in polished sections of carbonate rocks. Quartz can be detected in amounts $< 5\%$. For fine-grained rocks not subject to erratic incidence of strong reflection from individual large grains the method can be extended to semi-quant. or quant. estimates of abundance of the minerals present.

R. A. Howie

2442. **Deuterium content of minerals, rocks, and liquid inclusions from rocks.** N. Kokubu, T. Mayeda and H. C. Urey (Enrico Fermi Inst. for Nucl. Studies, Chicago Univ., Illinois). *Geochim. et Cosmoch. Acta*, 1961, **21** (3–4), 247–256.—In the method for the determination of the ^2H to H ratio of minerals and rocks, the combustion technique of Boato (*Ibid.*, 1954, **6**, 209) is used, with several modifications. Details are given for the extraction of water from the sample. The water is then passed over uranium metal at 600° to 800° to convert it into hydrogen, and the isotopic composition is measured with a 6-in. 60° mass spectrometer.

R. A. Howie

2443. **Micro-determination of nitrogen in rocks and silicate minerals by sealed-tube digestion.** F. J. Stevenson (Dept. of Agronomy, Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1704–1706.—Vycor-glass tubes and borosilicate-glass tubes are used, respectively, at above and below 420°. The finely ground sample (50 to 500 mg) and conc. H_2SO_4 (1·5 ml) are placed in the tube, which is sealed and then inserted in a protective iron casing and heated in a muffle-furnace. After opening the tube (behind a screen), gases are removed by heating the tube at 100° (for 15 min.) and N is recovered as NH_3 by a micro-Kjeldahl distillation, the final determination being made with Nessler soln. or by absorption in boric acid soln. (2%) and titration with 0·01N-H_2SO_4, with a mixed bromocresol green - methyl red indicator. Recommended minimum heating times (at 420°) are, for silicate minerals and igneous rocks, 90 min. and, for sedimentary rocks, 60 min. These times may be reduced by increasing the temp. The accuracy and precision of the method are considerably higher than when digestion is carried out in Kjeldahl flasks.

H. A. Foner

2444. **Estimation of cystine in acid zinc and Watts nickel baths by the a.c. polarographic method.** V. K. Venkatesan and S. Guruviah (Central Electrochem. Res. Inst., Karaikudi, India). *J. Sci. Ind. Res., India, B*, 1960, **19** (12), 496–498.—Since oxygen present in the soln. does not interfere with the a.c. polarographic reduction of cystine, the suitability of a modification of this technique for the rapid determination of cystine in plating baths has been studied. The apparatus described by Doss and Gupta (*Proc. Indian Acad. Sci., A*, 1952, **36**, 493), fitted with a saturated calomel electrode and a modified pool condenser (500 μF), was used. The concn. of cystine varied from 1·0 to 1·5 g per litre and 0·5 to 1·0 g per litre in acid zinc and Watts nickel baths, respectively. The soln. were buffered at pH 4·0 with an acetate - HCl buffer (0·1M with respect to Cl^-); a.c. polarograms and calibration curves for cystine in each type of bath are given. In acid zinc baths and Watts nickel baths, containing $\geqslant 2·5$ and 1·0 g of cystine, respectively, per litre, the concn. of cystine can be determined with an accuracy of $\simeq 4\%$. Advantages of the method are (*i*) that the soln. need not be de-aerated, (*ii*) that the complete polarogram need not be recorded and (*iii*) that the galvanometer does not require previous calibration.

I. A. Simpson

2445. **Nickel analyses of metallic meteorites by the electron-probe micro-analyser.** M. Feller-Kniepmeier and H. H. Uhlig (Metall. Dept., M.I.T., Cambridge, Mass., U.S.A.). *Geochim. et Cosmoch. Acta*, 1961, **21** (3–4), 257–265.—With the electron-probe micro-analyser a quant. analysis for Ni can be carried out in an area as small as 1 μ in diameter; composition is integrated to a depth of $< \simeq 1$ μ, hence errors caused by sub-surface inclusions are minimised. Specimen preparation is of the utmost importance. Any chemical treatment or etching results in high values for Ni; all specimens must therefore be polished with fine abrasives, any etching being done only after the analysis. Calibration is accomplished with 14 Fe - Ni alloys vacuum-melted from nickel carbonyl and electrolytic iron and homogenised in helium. The analyses for Ni are estimated to have a relative accuracy of $\pm 5\%$.

R. A. Howie

2446. **Field application of ion-exchange resins in hydrogeochemical prospecting.** F. C. Canney and D. B. Hawkins (U.S. Geol. Surv., Denver, Colo.). *U.S. Geol. Surv., Profess. Paper*, No. 400-B, 1960, 89–90.—Procedures are given for the purification of Amberlite IR-120 resin by alternate soaking in 6N-HCl and metal-free water, the preparation of the cartridge, the collection of the water sample and adjustment of its pH, if necessary, to between 6·5 and 7·5, and the elution of the metals. When 1-gall.

samples are used, an enrichment factor of 38 is obtained, permitting the detection by field colorimetric methods of 0·2 μg of Cu per litre, 1 μg of Pb and Zn per litre, and 0·5 μg of Co and Ni per litre. R. A. HOWIE

2447. **The sequential analysis of long-range fall-out debris.** G. A. Welford, W. R. Collins, jun., R. S. Morse and D. C. Sutton (Health and Safety Lab., U.S. Atomic Energy Comm., New York, U.S.A.). *Talanta*, 1960, **5** (3–4), 168–178 (in English).—The method permits the determination of the principal radionuclides of Sr, Ba, Ce, Cs, Y, Zr, Nb and W in single samples containing up to 10 g of inert substance. The sample, with added carriers, is fused with Na_2CO_3, and W and Cs are leached from the melt with hot water. An HCl leach removes Sr, Ba, Y, some rare-earth elements and part of the Zr and Nb; Sr and Ba are separated as the nitrates, and the remainder of the elements by anion-exchange adsorption. The radiometric and gravimetric recoveries are in the range 70 to 90%. W. T. CARTER

See also Abstracts—**2270**, Analysis in nuclear reactor technology. **2271**, *o*-Hydroxybenzenesulphinic acid as reagent for metals. **2280**, NH_4HSO_4 as fusion agent for spectrography. **2486**, Determination of hydrazine. **2555**, Se in plant material. **2632**, Al and Mg in magnesium aluminium silicate. **2664**, Chlorate in water.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather and explosives.

2448. **Recent developments in the ultra-micro analysis of organic compounds.** J. Berger (Royal Danish School of Pharm., Copenhagen). *Dansk Tidsskr. Farm.*, 1960, **34** (1), 4–14.—A review. P. PEDERSEN

2449. **EA-mass-spectrometric determination of the number of carbon atoms in organic molecules from the carbon-13 to carbon-12 ratio.** M. von Ardenne, K. Steinfelder and R. Tümmler (Forsch. Inst. Manfred von Ardenne, Dresden-Weisser Hirsch, Germany). *Naturwissenschaften*, 1960, **47** (21), 492–493 (in German).—Natural carbon contains 98·9% of ^{12}C and 1·1% of ^{13}C. As the number of C atoms in a molecule increases, so does the statistical probability (tabulated) that it will contain one or more ^{13}C atoms. The electron-addition ionisation technique (EA) of mass spectrometry permits the determination of the ^{13}C present, whence deductions can be made about the chemical composition of the sample. J. P. STERN

2450. **Micro-determination of carbon and hydrogen by a rapid automatic procedure.** L. Dorfman and G. I. Robertson (CIBA Pharm. Products, Inc., Summit, N.J.). *Anal. Chem.*, 1960, **32** (12), 1721.—A circuit is given for the automatic control of the movable furnace of the combustion apparatus described earlier (Robertson *et al.*, *Anal. Chem.*, 1958, **30**, 132). Modifications to the nitrogen oxide absorber and the absorption tubes are described. R. M. ROWLEY

2451. **Semi-micro manometric method for the determination of carbon and hydrogen in organic compounds.** R. L. Scott, J. E. Puckett, H. A. Price, M. D. Grimes and B. J. Heinrich (Philips Petroleum Co., Bartlesville, Okla., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (5), 428–433 (in English).—Advantages in speed and accuracy are claimed for the method. Combustion takes place in a modified Pregl furnace, and H_2O and CO_2 are collected in solid CO_2 and liquid-nitrogen traps, respectively. They are then separately vaporised into an evacuated mercury manometer held at 70° ± 0·02°. Hydrogen and C contents are derived from the observed pressures by means of calibration graphs. Oxides of N are removed with activated MnO_2. H. N. S.

2452. **Effective tube-fillings for the determination of carbon and hydrogen.** G. Kainz and H. Horwatitsch (Anal. Inst., Univ. Wien, Austria). *Z. anal. Chem.*, 1960, **177** (5), 321–327 (in German).—The effect of CuO, MnO_2 and Co_3O_4 in the combustion of methane in a stream of O and CO_2 has been studied. It is shown that their oxidising capacity depends on the surfaces of the pptd. catalysts and increases from CuO to Co_3O_4. The tube-filling consists of a 2·5-cm layer of the appropriate oxide, and combustion curves show that methane is quantitatively oxidised by Co_3O_4 at 345°, by MnO_2 at 410°, and by CuO at 445°. B. B. BAUMINGER

2453. **Oxidising efficiency of mixed catalysts in the determination of carbon and hydrogen.** G. Kainz and H. Horwatitsch (Anal. Inst., Univ. Wien, Austria). *Z. anal. Chem.*, 1960, **177** (5), 344–352 (in German).—Five mixtures of combustion catalysts, namely, coarse CuO impregnated with Cr_2O_3, Co_3O_4 or Ag, and Co_3O_4 - asbestos and the decomposition product of $AgMnO_4$, have been studied for their efficiency in the combustion of methane in oxygen. It is shown that the oxidising efficiency of the mixed catalysts is equal to that of a single component, and that above 450° the mixture forms a less active compound with reduced efficiency. The catalyst CuO - Co_3O_4 is effective at 440° and is recommended for determinations of C and H; it is prepared by mixing 21 g of coarse CuO with 1 g of $Co(NO_3)_2.6H_2O$ in water. The product is evaporated to dryness and de-nitrated at 500°. B. B. BAUMINGER

2454. **Micro-determination of active hydrogen with tritiated ethanol.** J. A. Giles (R. J. Reynolds Tobacco Co., Winston-Salem, N.C., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1716–1717.—The sample (0·1 milli-equiv.) is dissolved in [^{3}H]ethanol, and toluene is added. The excess of ethanol is removed by distillation and the soln. is made up to a known volume with a soln. of a scintillator. The activities of aliquot portions of the soln. are then measured, and compared with those of the [^{3}H]ethanol. The method has been applied to a variety of non-volatile compounds. R. M. ROWLEY

2455. **The application of colorimetry in non-aqueous media to the determination of organic functional groups.** M. Pesez and J. Bartos (Centre de Rech., Roussel-Uclaf, Paris, France). *Talanta*,

1960, **5** (3–4), 216–220 (in French).—Chromogenic reactions are based on the formation of derivatives with reagents containing aromatic nitro-groups, which give characteristic colours when treated with an organic base in dimethylformamide soln. The removal of excess of reagent is unnecessary. Procedures are given for primary and secondary alcohols with 3,5-dinitrobenzoyl chloride and piperazine, for ketones with *p*-nitrophenylhydrazine and benzyltrimethylammonium hydroxide (**I**), and for primary aliphatic amines with 1-fluoro-2,4-dinitrobenzene and **I**. Primary aliphatic amines can also be detected by condensing with *p*-dimethylaminocinnamaldehyde in nitromethane. The reactions are suitable for the determination of ≃ 20 to 100 μg. W. T. CARTER

2456. **Studies on organic micro-analysis. IX. Sensitive detection of alkoxyl groups.** Minoru Fukuda (Pharm. Fac., Univ., Osaka, Japan). *Chem. Pharm. Bull., Japan*, 1960, **8** (11), 1054–1055.—The alkoxyl groups are converted into alkyl iodide by a modified Pregl method. The alkyl iodide is then burnt and the liberated iodine is detected with starch. The reagent mixture is prepared by heating HI (sp. gr. 1·7) (100 g), propionic acid (5 to 10 g), phenol (60 g) and a little red phosphorus under reflux for 1 to 1·5 hr. in a stream of CO_2; the supernatant liquid is used. *Procedure*—Mix the sample (≃ 50 μg) and the reagent mixture (1 ml) in the apparatus previously described (*Japan Analyst*, 1960, **80**, 25). Attach a gas-testing tube (*loc. cit.*) containing 4 drops of starch soln. (0·05%, preserved with HgI_2) and heat for 10 min. The starch soln. turns blue in the presence of alkoxyl groups; 3 μg of methoxyl and 5 μg of ethoxyl may be detected. Alcohols also give a positive result. G. RUSSELL

2457. **Determination of carboxyl groups.** K. Christofferson and O. Samuelson (Dept. Engng Chem., Chalmers Tekniska Högskola, Göteborg, Sweden). *Svensk Papp-Tidn.*, 1960, **63** (21), 749–751 (in English).—A method for the determination of carboxyl groups, devised by Samuelson and Wennerblom (*Ibid.*, 1955, **58**, 713), gives good reproducibility with samples that are stable in alkaline soln. This method gives higher values than other methods commonly used, and the difference is explained by an incomplete reaction in the latter methods. The present method can be used only on samples with a very low carbonyl content. P. PEDERSEN

2458. **Gas-chromatographic analysis of hydrogen - methane mixtures using the radioactive ionisation detector.** A. K. Galwey (Queen's Univ., Belfast, N. Ireland). *Chem. & Ind.*, 1960, (46), 1417–1418.—Under the conditions described, when H enters the detector a deflection is given in the opposite direction to that given by compounds having an ionisation potential of < 11·7 eV. Since methane behaves normally, it is necessary to operate the recorder with a base line at ≃ 85% of the full-scale deflection for the measurement of the H trough, before changing to ≃ 15% for the elution of methane. A 2-ft. column of activated charcoal (100 to 200 mesh) with an Ar flow of 30 ml per min. was used. G. P. COOK

2459. **Chromatographic separation of hydrogen, paraffins and olefins with flame-detector indication.** V. Kusý (Stalinovy Závody, Záluží v Krušných Horách, Czechoslovakia). *Chem. Listy*, 1960, **54** (11), 1168–1172.—The procedure of Wirth ("Vapour Phase Chromatography," Butterworths Sci. Publ., London, 1957, p. 154) was used for micro-flame detection in a new apparatus for chromatographic analysis, by which H and paraffins or olefins (C_1 to C_6) can be determined simultaneously by registering the temp. of combustion of the components. The use of air as carrier gas ensures the complete combustion of hydrocarbons. Quantitative evaluation was carried out by the use of the planimetric method. J. ZÝKA

2460. **Determination of ethylene in a methane - hydrogen mixture.** E. M. Kulik. USSR Pat. 131,543 (10.9.1960).—The ethylene is continuously hydrogenated to ethane by the H in the mixture in the presence of a palladium catalyst, and the ethane is determined by i.r. absorption. The total error is 5% of the max. scale reading. C. D. KOPKIN

2461. **Some refinements in the correlations of the Raman spectra with molecular structures for acyclic mono-olefinic hydrocarbons.** D. G. Rea (California Res. Corp., Richmond, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1638–1651.—The Raman spectra of more than 60 olefins have been recorded. The position, band width, integrated intensity and peak intensity of the C = C stretching band at ≃ 1650 cm^{-1} have been measured for each compound. The CH_2 deformation band at ≃ 1380 cm^{-1} has also been studied. There is considerable interaction between the C = C stretching and CH_2 deformation modes when the groups C:C·CH_2 or C:C·C·CH_2 are present. The positions of other characteristic bands are also given, and a comparison is made with the data of other authors. R. M. ROWLEY

2462. **Analytical control of isoprene rectification.** Z. Dolejšek, O. Grubner, V. Hanuš, I. Kössler, B. Matyska and J. Vodehnal (Inst. Phys. Chem., Acad. Sci., Prague). *Chem. Průmysl*, 1960, **10** (11), 571–576.—Samples of technical isoprene (96% and 13%) containing butenes, pentenes and traces of hexenes as impurities were studied by gas chromatography, mass spectrometry and i.r. spectroscopy during the distillation processes. The advantages and limitations of the methods are discussed. J. ZÝKA

2463. **A classification test for alkyl halides.** R. L. Dannley and F. V. Kitko (Morley Chem. Lab., Western Reserve Univ., Cleveland, Ohio). *Anal. Chem.*, 1960, **32** (12), 1682–1684.—Dissolve the halide (0·5 ml) in 1·5 ml of dimethylformamide containing $NaNO_2$ (30 g per litre) and urea (50 g per litre). Allow iodides to stand for 20 min.; heat bromides and chlorides on a water bath for 15 min. Add 10% aq. $NaNO_2$ soln. (1 ml) and 10% NaOH soln. (2 ml), and shake the mixture. Add CCl_4 (1 ml), then 10% H_2SO_4 (1·5 ml) dropwise, with shaking. If the aq. layer turns a tan colour, a primary halide is indicated. Add 10% acetic acid dropwise until the CCl_4 layer turns blue or 3 ml of acid has been added. The blue colour indicates a secondary halide. If no colour develops a tertiary halide is indicated. R. M. ROWLEY

2464. ***N*-Substituted imides. II. Potassium naphthalimide as a reagent for the identification of alkyl halides.** M. A. Devereux and H. B. Donahoe (Univ. St. Louis, Mo., U.S.A.). *J. Org. Chem.*, 1960,

25 (3), 457–458.—Alkyl halides can be identified by the m.p. of their *N*-alkylnaphthalimides. The preparation proceeds smoothly with primary and secondary chlorides, bromides and iodides, but yields are low with secondary halides. Tertiary halides do not react. *Procedure*—To a flask containing 2·35 g (0·01 mole) of K naphthalimide add 0·01 mole of alkyl halide and 15 ml of dimethylformamide. Heat under reflux on a steam bath for 1 hr., cool and filter off the ppt. of potassium halide. Treat the filtrate with cold water, filter off the ppt. of *N*-alkylnaphthalimide, and dissolve it in ethyl ether. Remove any insol. matter, evaporate off the ether and recrystallise the residue; m.p. and suitable solvents for recrystallisation are tabulated for 17 derivatives. R. E. E.

2465. **Analytical application of chemiluminescence of biacridyl derivatives. I. Identification of some aliphatic alcohols.** E. Michalski and M. Turowska (Dept. of Inorg. Chem., Univ., Łódź, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 625–630.—The catalytic action of methanol, ethanol, propanols and t-butyl alcohol on the chemiluminescence of biacridyl derivatives is used to identify the alcohols. The quenching or excitation of chemiluminescence occurs at a fixed pH which depends on the concn. and nature of the alcohol. Both the methyl (lucigenin) and ethyl derivatives are suitable, and the pH value is conveniently varied by the addition of one of the components of a phosphate buffer. Pure alcohols or their aq. soln. (after dehydration) can be identified.

II. Determination of methanol and ethanol in mixtures. E. Michalski and M. Turowska. *Ibid.*, 1960, **5** (4), 631–636.—The pH value at which chemiluminescence is excited or quenched varies directly with the proportion of the two alcohols in an anhydrous mixture, thus giving a semi-quant. method for their determination with an accuracy of $\simeq$ 10%. P. Brych

2466. **Photometric determination of alcohols by means of vanadium 8-hydroxyquinolinate.** Motoharu Tanaka (Lab. of Anal. Chem., Fac. Sci., Univ. Nagoya, Japan). *Talanta*, 1960, **5** (3–4), 162–167 (in English).—Vanadium 8-hydroxyquinolinate reacts with alcohols to give a red complex which can be measured spectrophotometrically at 635 mμ. *Procedure*—To the sample soln. (5 ml, in $CHCl_3$ or nitrobenzene) containing up to 50 μmoles of alcohol add 0·1% vanadium hydroxyquinolinate soln. in the same solvent. With nitrobenzene soln., heat at 70° for 10 min. With $CHCl_3$ soln., set aside at room temp. for 3 hr. Measure the extinction at 635 mμ. The complex is stable for at least 24 hr. in the presence of excess of reagent. The sensitivity is greatest in solvents of low dielectric constant and depends on the reactivity of the hydroxyl group of the alcohol. W. T. Carter

2467. **Separation and identification of glycidyl ethers by gas chromatography.** V. Ulbrich and O. Dufka (Res. Inst. Synth. Resins, Pardubice, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (10), 549–554.—The chromatographic column was filled with methyl silicone oil on kieselguhr. Hydrogen was used as the carrier gas and thermal-conductivity detection for the evaluation of the results. Eighteen different glycidyl ethers were examined, their specific elution vol. determined and mixtures analysed. J. Zýka

2468. **An improvement to the lead tetra-acetate detection of sugar alcohols in paper electrophoresis.** K. Sampson, F. Schild and R. J. Wicker (Howards of Ilford Ltd., Ilford, Essex). *Chem. & Ind.*, 1961, (3), 82.—The usual electropherogram consisting of white to pale-brown spots on a brown background of PbO_2 is improved by treatment with a 0·03% soln. of rosaniline base in a mixture of glacial acetic acid and acetone (1:9). The rosaniline is oxidised by the PbO_2 to give a pale-grey colour and produces red spots with the aldehydes formed by oxidation of the alcohols. Sorbitol (0·4 μg) can be detected by this method. N. E.

2469. **Determination of reducing sugars with 3,6-dinitrophthalic acid.** Tsutomu Momose, Yoshiko Mukai and Mitsuko Watanabe (Pharm. Inst., Med. Fac. Univ., Kyushu, Fukuoka, Japan). *Talanta*, 1960, **5** (3–4), 275–277 (in English).—Reducing sugars (10 to 100 μg per ml) are determined spectrophotometrically by the method previously described (*cf.* Momose *et al.*, *Anal. Abstr.*, 1960, **7**, 4919). The calibration curves for xylose and arabinose, for glucose, fructose and galactose, and for lactose and maltose coincide with each other, indicating that the configuration of the hydroxyl groups in the sugars does not affect the reduction. Mixtures of glucose and sucrose can be analysed with an error of $\simeq$ 3% by determining glucose on one aliquot and total invert sugar on a second aliquot after inversion with 0·1N-HCl. W. T. Carter

2470. **Amperometric determination of glucose, fructose and sucrose at zero applied potential.** E. Michalski, K. Czarnecki and M. Ignaczak (Inorg. Chem. Dept., Univ. Łódź, Poland). *Talanta*, 1960, **5** (3–4), 137–140 (in English).—The sugars are oxidised to formic acid and CO_2 by an excess of 0·1N-$Ce(ClO_4)_4$ in N-$HClO_4$ at 60° for 35 to 50 min. After cooling the soln., the excess of oxidant is determined by back-titration with 0·15N-Na oxalate in N-$HClO_4$. The end-point is detected with bright platinum and satd. calomel electrodes connected to a galvanometer with a sensitivity of 3×10^{-7} amp. per scale division. No potential is applied, but the soln. is stirred vigorously during the titration. For 10 to 12 replicate determinations the standard deviation varies from $\simeq$ 0·01 mg for $<$ 1 mg of the individual sugars to $\simeq$ 0·02 mg for 10 mg. W. T. Carter

2471. **Separation of sugars on ion-exchange resins. I. Separation of oligosaccharides.** J. K. N. Jones, R. A. Wall and A. O. Pittet (Queen's Univ., Kingston, Ontario, Canada). *Canad. J. Chem.*, 1960, **38** (12), 2285–2289.—Synthetic mixtures of oligosaccharides, and various polysaccharide hydrolysates, were separated on columns of the neutral salt forms of cation-exchange resins. The separation depends on molecular size; the equilibria between polyhydric compounds and ion-exchange resins have been studied by Wheaton and Bauman (*Ann. N.Y. Acad. Sci.*, 1953, **57**, 159) and Samuelson *et al.* (*Acta Chem. Scand.*, 1958, **12**, 1386, 1404). The most satisfactory resin was Dowex 50W-X2 (200 to 400 mesh, Li^+ form), and the separation of 100-mg amounts was complete in 24 to 48 hr., with water as the developing solvent. Details are given of the separation of synthetic mixtures of raffinose and melibiose, of D-glucose and maltose, and of lactose and D-galactose. Recoveries were 97 to 105%. *O*-Alkylated monosaccharides were separated by the same method.

II. Separation of monosaccharides. J. K. N. Jones and R. A. Wall. *Ibid.*, 1960, **38** (12), 2290–2294.—Synthetic mixtures of monosaccharides were separated on a column of Dowex 50W-X8 (200 to 400 mesh, Ba^{2+} form), with water as the developing solvent. The volumes of eluate at which max. concn. of the given sugar is attained are tabulated for 18 sugars for elution from a column (70 cm × 2·2 cm); the practicability of separating two or more sugars can thus be assessed. For amounts of 50 mg to 1 g, the recovery was usually 90 to 95%. Details are given of the complete separation of D-xylose and D-ribose, and the partial separation of D-glucose and D-galactose. Several sugars were resolved from plant extracts (*Sedum* spp. and avocado fruit), and the epimerisation products of D-galactose were separated. C. S. HOWES

2472. **Detection of some deoxy-sugars and aldehydes using thiobarbituric acid.** L. D. Saslaw and V. S. Waravdekar (Armed Forces Inst. Path., Washington, D.C., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **90** (2), 245–249.—The compounds (0·1 to 25 μg) are detected on filter-paper by spraying with 0·6% thiobarbituric acid soln. (pH 2). The paper is then sandwiched between glass plates and heated at 90° for 5 min. before examination visually and under u.v. light and after treatment with NH_3 vapour. For the detection of deoxy-ribosyl and other compounds yielding aldehydes on oxidation, the paper is sprayed with 0·04M-$NaIO_4$. After 10 min. the paper is sprayed with 3·5% $NaAsO_2$ soln. in N-HCl and again after 2 min. Thiobarbituric acid treatment follows after a further 2 min. W. H. C. SHAW

2473. **Staining of polysaccharides on electropherograms.** A. E. Greiser (Pavlov Med. Inst., Leningrad). *Lab. Delo*, 1960, **6** (6), 48–51.—Covered Plexiglas cells, the same length as the electropherogram and sufficiently wide to accommodate two strips, are used as dye baths. The cells are wrapped in black paper. The strips are placed in oxidising agent [KIO_4 (0·8 g) dissolved in 96% ethanol (70 ml) containing conc. HNO_3 (0·3 ml), 0·2M-Na acetate (hydrated) soln. (10 ml) and H_2O (20 ml)] for 12 min., washed in running water for 2 to 3 min., immersed in freshly prepared reducing agent [KI (2 g) and $Na_2S_2O_3.5H_2O$ (2 g) dissolved in 96% ethanol (60 ml) containing H_2O (40 ml) and N-HCl (2 ml)] for 10 to 20 sec., washed in running water for 5 min. and placed in Schiff's reagent for 15 to 20 min., or longer if necessary, and washed in water. The strips are either dried in air or with acetone. On drying, the pink background fades and the zones deepen to a purple-red colour. K. R. COOK

2474. **Determination of aldehydes from hemi-acetal formation.** J. S. Forrester (Esso Res. Lab., Humble Oil and Refining Co., Baton Rouge, La.). *Anal. Chem.*, 1960, **32** (12), 1668–1670.—The absorption in the u.v. of soln. of aldehydes in alcohols increases with increase in temperature, because of the lowering of the proportion of the aldehyde present as the hemi-acetal. By measuring the difference between the extinctions at 25° and at 100°, at 290 mμ, the aldehyde can be determined in the presence of other absorbing substances. It was found that 0·2 to 15 g of C_{10} aldehyde per litre in C_{10} alcohol could be determined in the presence of a phenolic inhibitor. The method is suitable for continuous stream analysis. R. M. ROWLEY

2475. **Amperometric determination of acetaldehyde with hydroxyammonium chloride.** R. E. Van Atta, W. W. Harrison and D. E. Sellers (Dept. of Chem., Southern Illinois Univ., Carbondale, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1548–1550.—Acetaldehyde soln. (1 to 100mM) in 0·1M-KCl can be titrated with 0·1M-hydroxyammonium chloride by following the increase in current due to the reduction of the oxime at the dropping mercury cathode. The cathode potential is kept at −1·25 V *vs.* the S.C.E.; at this potential neither impurities such as ethanol, ethyl acetate or acetic acid, nor acetaldehyde or hydroxylamine are reduced. Acetone interferes if its concn. is > 40% of that of the acetaldehyde. The relative deviation of a single determination is ≃ 1%. R. M. ROWLEY

2476. **Determination of mixtures of butyraldehydes and butyl alcohols.** M. Šingliar, J. Brida and A. Bobák (Res. Inst. Petrochem., Nováky, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (10), 530–532.—Gas-liquid chromatography was used for the determination of mixtures of iso- and n-butyraldehydes with isobutyl alcohol and n-butanol. The best results were obtained with diethylene glycol dibenzoate (16·6%) on kieselguhr at 100°, with N as the carrier gas and thermal-conductivity detection. The interference of the moisture in the sample can be avoided by placing a 2-cm layer of calcium carbide at the entrance of the column. An accuracy of ± 1·5% was achieved. J. ZÝKA

2477. **Polarographic studies on concentrated acetaldehyde solutions and determination of crotonaldehyde in technical acetaldehyde.** J. Paściak (Chem. Works, Oświęcim, Poland). *Chem. Anal., Warsaw*, 1960, **5** (5), 797–807.—*Procedure*—To the polarographic cell add 5 ml of 0·25N-HCl-0·25N-LiCl (1:1) containing 0·03% of gelatin and 0·50 ml of sample. Remove O by a stream of N and perform the determination at 10° at a pH < 2·3; the $E_{\frac{1}{2}}$ *vs.* the S.C.E. = ≃ −1·1 V. Treat the standard soln. by the same procedure. The accuracy is ± 1%, and as little as 0·001% of crotonaldehyde in acetaldehyde can be determined. B. K.

2478. **Determination of traces of isopropyl alcohol and water in acetone by infra-red spectrophotometry in non-polar solvents.** M. Desnoyer (Dept. de Phys.-chim., Centre d'Études Nucleaires, Saclay). *Bull. Soc. Chim. France*, 1960, (10), 1754–1756.—The i.r. spectra of samples of acetone which have been treated with powdered nickel suggest the presence of water and isopropyl alcohol. The i.r. spectrum of acetone is such that only the water content can be determined by means of the band at 3600 cm^{-1}. In CCl_4 an alcohol concn. < 0·01M can be determined by measurement of the intensity of the band at 3630 cm^{-1}. At higher concn. (0·15M) the isopropyl alcohol content has been determined in CS_2 soln. by means of the band at 950 cm^{-1}. E. G. CUMMINS

2479. **Some physical characteristics of the 2,4-dinitrophenylhydrazine and semicarbazide derivatives of three-carbon carbonyls.** J. C. Underwood and H. G. Lento (Eastern Regional Res. Lab., Agric. Res. Service, U.S. Dept. of Agric., Philadelphia 18, Pa.). *Anal. Chem.*, 1960, **32** (12), 1656–1658.—I.r. and u.v. absorption spectra of

the 2,4-dinitrophenylhydrazones of acetol (hydroxyacetone), dihydroxyacetone and glyceraldehyde are presented. U.v. absorption spectra of the semicarbazones of hydroxyacetone and pyruvaldehyde are also presented. The m.p. of all these derivatives, and of the osazones of pyruvaldehyde and hydroxypyruvaldehyde, are given.

R. M. ROWLEY

2480. **Improved methods for the paper chromatography of organic acids.** R. D. Hartley and G. J. Lawson (Dept. of Mining and Minerals Engng, Univ., Birmingham, England). *J. Chromatography*, 1960, **4** (5), 410–413 (in English).—Six solvent mixtures have been found advantageous for the separation of organic acids. Three are acid mixtures containing ethyl acetate or formate, acetic or formic acid, water, and Na acetate or formate (0·05%); one is a basic mixture of ethanol and aq. NH_3; and two are buffered ethanol. All the solvents contain indicator, *viz*, bromophenol blue in the acid, thymol blue in the basic, and chlorophenol red in the buffered solvents. All are suitable for one- or two-dimensional chromatography.

G. BURGER

2481. **Preparation [and determination] of peroxyacetic acid.** S. Havel, J. A. Weigner and J. Šváb (Inst. Chem. Technology, Pardubice, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (11), 579–581.—The following method of determination is recommended. Dissolve the sample (0·6 to 0·8 g) in 100 ml of ice-cooled H_2O, add 10 ml of this soln. to a mixture of a satd. soln. of KI in 0·1N-acetic acid (50 ml) containing ammonium molybdate soln. (3%) (3 drops), close the flask and after 15 min. titrate the free iodine with 0·1N-$Na_2S_2O_3$, with starch as indicator.

J. ZÝKA

2482. **Rapid spectrophotometric assay of α,β-unsaturated acids and β-hydroxy-acids.** R. A. Slepecky and J. H. Law (Dept. of Biol. Sci. and Chem., Northwestern Univ., Evanston, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1697–1699.—The absorption maximum of soln. of α,β-unsaturated acids in H_2SO_4 occurs in the region 215 to 250 mμ, and can be used for their determination. Neither the position of the maximum nor the intensity of the absorption varies much with H_2SO_4 concn. in the range 80 to 100% (v/v). β-Hydroxy-acids can be determined by heating with conc. H_2SO_4 at 100° for 10 min. and measuring the extinction of the α,β-unsaturated acids that are formed. The method has been used for the determination of crotonic and β-hydroxybutyric acids (at 235 mμ), β-methylcrotonic and mevalonic acids (at 251 mμ), and acrylic acid (at 216 mμ). Triplicate determinations agreed to within 5%. The minimum detectable amount is $\simeq 10^{-6}$ mole ($\epsilon = \simeq 10^4$). Sugars interfere, but glycerol, ethyl acetoacetate and α-hydroxybutyric acid have little effect on the determination.

R. M. ROWLEY

2483. **Separation of hydroxy-acids by ion-exchange chromatography.** B. Alfredsson, L. Gedda and O. Samuelson (Dept. Engng Chem., Chalmers Tekniska Högskola, Göteborg, Sweden). *Svensk Papp-Tidn.*, 1960, **63** (21), 758–761 (in English).—The following hydroxy-acids can be separated from each other by means of chromatographic elution with $Na_2B_4O_7$ soln. on a Dowex 1-X8 column—3,4-dihydroxybutyric acid, 3-deoxythreopentonic acid, α-D-isosaccharic acid, β-D-glucometasaccharic acid and α-D-glucosaccharic acid. The method can also be applied to the quantitative determination of these acids in mixtures with glycollic and lactic acids. The separation of glycollic and lactic acids from each other is incomplete under the conditions given.

P. PEDERSEN

2484. **Acidimetric determination of 2,3:4,6-di-O-isopropylidene-2-oxo-L-gulonic acid in non-aqueous medium.** M. Konupčík, M. Liška and F. Kupčík (Dept. Tech. Control, Farmakon, Olomouc, Czechoslovakia). *Českosl. Farm.*, 1960, **9** (10), 516–517.—*Procedure* (*i*)—Dissolve the sample (1 g) by shaking for 10 min. with $CHCl_3$ (60 to 70 ml) and dilute with the same solvent to a known vol. Filter through paper and to 50 ml of filtrate add solid phenolphthalein as indicator and titrate with 0·1N-Na methoxide till the soln. is slightly pink. (*ii*)—To the sample (0·5 to 0·6 g) in a sintered glass crucible (S3) add $CHCl_3$ (20 ml) and, after allowing it to drip through for 2 min., remove any remainder with gentle suction. Repeat this procedure four times. To the $CHCl_3$ soln. add phenolphthalein and proceed as described in (*i*). The error is ± 0·5%. Oxalates do not interfere, as they are insoluble in $CHCl_3$ and can be removed by filtration.

J. ZÝKA

2485. **Relative detector response in gas chromatography. III. Aliphatic esters.** G. R. Jamieson (Tech. Coll., Paisley, Scotland). *J. Chromatography*, 1960, **4** (5), 420–422 (in English).—The response of a thermal-conductivity detector (relative to benzene) has been determined for a large number of aliphatic esters. The results are listed. The response increases with increasing mol. wt., regularly in homologous series. Isomeric esters have a similar response if there is no branching. Branching decreases the response. The position of substituent groups has a large effect. The response is also affected by the nature of the substituent. Unsaturated esters have a lower response than saturated esters of the same mol. wt. The position of the double-bond has little effect.

G. BURGER

2486. **Coulometric determination of hydrazine and substituted hydrazines.** E. C. Olson (The Upjohn Co., Kalamazoo, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1545–1547.—Hydrazine and many substituted hydrazines react rapidly and stoicheiometrically with electrolytically generated bromine in methanol - water - acetic acid soln. containing mercuric acetate and KBr. Hydrazine and monosubstituted hydrazines react with 4 equiv. of Br, but unsymmetrically disubstituted hydrazines consume 6 equiv.; the reactions of symmetrically disubstituted compounds are variable. With a generating current of 20 mA through platinum-foil electrodes 1 sq. cm in area, and platinum-wire indicating electrodes with 200 mV applied potential, determinations of 3 to 5-mg samples of pure (2-*o*-methoxyphenyl-1-methylethyl)hydrazine gave a coeff. of variation of 0·8%.

R. M. ROWLEY

2487. **Chloramine T as volumetric reagent: determination of organic derivatives of hydrazine.** Balwant Singh, S. S. Sahota and R. P. Singh (Punjab Univ., Chandigarh, India). *J. Indian Chem. Soc.*, 1960, **37** (7), 392–394.—The method has been used for the determination of semicarbazide hydrochloride (**I**), 4-phenylsemicarbazide hydrochloride (**II**), thiosemicarbazide, benzaldehyde semicarbazone and its *o*- and *m*-nitro-,

o-hydroxy-, *p*-methoxy-, and *o*- and *p*-chloro-derivatives, acetone semicarbazone, benzoylhydrazine, benzaldazine, phenylhydrazine hydrochloride and 1-formyl-2-phenylhydrazine. *Procedure*—Dissolve the sample (≃ 50 mg) in aq. HCl (≃ 40 ml), add 0·02M-ICl (5 ml) and $CHCl_3$ (5 ml), cool to room temp. and titrate with 0·05M-chloramine T, with vigorous shaking, until the $CHCl_3$ layer changes from purple to pale yellow. The concn. of HCl must be maintained between 0·7N and 1·0N for **I** and **II**, and between 2·5N and 4·5N for all the other compounds. Alternatively, titrate potentiometrically (platinum and satd. calomel electrodes) with 0·05M-chloramine T in 5N to 5·5N-HCl, with the addition of 0·005M-KI (one drop) as catalyst.

A. R. ROGERS

2488. **Infra-red spectra of ethylenediamine dihydrochloride and other amine hydrochlorides in alkali halide discs.** J. Bellanato (Inst. of Optics, Madrid, Spain). *Spectrochim. Acta*, 1960, **16** (11–12), 1344–1357 (in English).—Differences observed in the spectra of discs prepared with KCl, KBr, KI, NaCl and NaBr are discussed. It is concluded that the changes are mainly produced by hydrogen-bond-type interactions between the physically adsorbed polar molecules and the negative ions Cl^-, Br^- and I^- of the polycrystalline alkali halides.

E. G. CUMMINS

2489. **Complexometric determination of copper in copper ethylenediamine solutions.** J. Šára and W. Berndt (Spolana n.p., Neratovice, Czechoslovakia). *Svensk Papp-Tidn.*, 1960, **63** (16), 528–530 (in German).—A direct titration method is described. The test soln. is buffered with Na acetate and titrated with EDTA (disodium salt), with xylenol orange or methylthymol blue as indicator.

P. PEDERSEN

2490. **Ultra-violet absorption of aliphatic nitro-compounds in the presence of a base.** J. H. Gast and F. L. Estes (Baylor Univ. Coll. of Med., Houston 25, Tex.). *Anal. Chem.*, 1960, **32** (12), 1712–1713.—The extinction of aliphatic nitro-compounds in alkaline soln. at ≃ 300 mμ cannot be used for their determination. The extinction varies with time, and the extinction coeff. varies with concn.

R. M. ROWLEY

2491. **Estimation of aliphatic thiocarbamides [thioureas]. II. *N*-Methylthiocarbamides [*N*-methylthioureas].** Prakash Chandra Gupta (Coll. of Sci., Benares Hindu Univ., Varanasi). *J. Indian Chem. Soc.*, 1960, **37** (10), 629–633.—The iodimetric methods described previously (*Anal. Abstr.*, 1961, **8**, 172) for the determination of thiourea have been extended to the determination of the various mono-, di-, tri- and tetra-methylthioureas. The accuracy is generally better than ± 1%. An excess of KI must be present in the titration of tetramethylthiourea; each molecule consumes only 3 molecules of iodine and not 4 molecules as do the other derivatives.

A. R. ROGERS

2492. **Detection of monobasic phosphorus acid esters by conversion to cholinesterase inhibitors.** H. W. Yurow, D. H. Rosenblatt and J. Epstein (Biochem. Res. Div., U.S. Army Chem. Warfare Lab., Army Chem. Center, Maryland, U.S.A.). *Talanta*, 1960, **5** (3–4), 199–204 (in English).—Esters of monobasic acids of quinquevalent phosphorus applied to filter-paper can be converted into cholinesterase inhibitors by exposure to ketene. These inhibitors are detected by a modification of the method of Cook (*J. Ass. Off. Agric. Chem.*, 1955, **38**, 150), in which the paper is sprayed with a soln. containing horse serum (source of cholinesterase), acetylcholine and bromothymol blue. The sensitivity varies from 0·02 to 1 μg of ester per sq. cm of paper. Of the 36 phosphorus compounds tested, 17 gave positive results, of which 16 were esters of monobasic acids and 1 was an ester of a dibasic acid.

W. T. CARTER

2493. **Infra-red and Raman spectra of dimethyl- and trimethyl-silanes and some deuterated derivatives.** D. F. Ball, P. L. Goggin, D. C. McKean and L. A. Woodward (Dept. of Chem., Aberdeen Univ., Scotland). *Spectrochim. Acta*, 1960, **16** (11–12), 1358–1367 (in English).—The results reported suggest that coupling between bending motions of SiH and SiH_2 groups and other motions prevents the assignment of SiH bending modes. Otherwise complete assignments have been made.

E. G. CUMMINS

2494. **Quantitative analysis of mixtures of organometallic compounds of lead.** R. Barbieri, U. Belluco and G. Tagliavini (Ist. Chim. Gen., Univ., Padova, Italy). *Ric. Sci.*, 1960, **30** (11), 1671–1674.—The quant. analysis of mixtures of organo-lead compounds of the types R_3PbCl, R_2PbCl_2 and R_4Pb, where R may be ethyl, methyl or phenyl, is effected by paper-chromatographic separation followed by conversion into $[PbI_4]^{2-}$, which are then determined spectrophotometrically at 357 mμ. A calibration curve is prepared for soln. of PbI_2 in 4M-KI containing 2 to 16 μg of Pb per ml. The curve is not quite rectilinear but the error at 16 μg of Pb per ml is ≯ 2%. Soln. of the individual compounds (0·1 to 1·0 ml, containing 20 to 160 μg of Pb per ml) were mixed with 3 vol. of ethanol saturated with iodine. After 5 min. the mixtures were evaporated to dryness on a water bath, the iodine was removed by heating on a hot-plate, and the residue was dissolved in 4M-KI to 10 ml and examined spectrophotometrically against 4M-KI. The last traces of iodine were removed with a drop of 0·1M-$Na_2S_2O_3$. Recoveries of Pb ranged from 98 to 102·2% of the theoretical. The solvents used for the di- and tri-methyl- and di- and tri-ethyl-lead chlorides were H_2O and methanol; for the di, tri- and tetra-phenyl compounds, $CHCl_3$, acetone or methanol; and for the tetramethyl and tetraethyl compounds, n-heptane. Mixtures of di- and tri-methyl- and di- and tri-ethyl-lead chlorides with $PbCl_2$, containing 25 to 40 μg of total Pb per ml, were separated chromatographically on paper (*Ann. Chim.*, 1958, **48**, 940), the spots, located by means of a reference strip, being then cut out and extracted, the extracts being treated as described above. The errors ranged from − 2·0 to + 1·9%. Treatment of the spots on the paper without previous elution was more rapid but less precise, the errors amounting to as much as 12·5%. Ionic Pb present as an impurity was determined by dissolving the sample in H_2O, adding KI to a concn. of 4M and reading the extinction at 357 mμ, the organo-lead compounds having no absorption at this wavelength; the Pb^{2+} are converted into $[PbI_4]^{2-}$. Alternatively, the Pb^{2+} can be titrated photometrically at 240 mμ with a standard soln. of EDTA, the organo-lead compounds showing no interference.

J. I. M. JONES

2495. **Analysis of organometallic compounds of lead.** U. Belluco, G. Tagliavini and R. Barbieri (Ist. Chim. Gen., Univ., Padova, Italy). *Ric. Sci.*, 1960, **30** (11), 1675–1679.—Hexaethyldilead (**I**) reacts with $AgNO_3$ to give metallic silver, which can be separated, dissolved in HNO_3 and titrated by Volhard's method. Tetraethyl-lead (**II**) reacts similarly so that the method is not suitable for mixtures of these compounds. **I** can also be determined by dissolving the sample in CCl_4, covering the soln. with H_2O containing starch indicator and titrating in an atmosphere of N with 0·01N-iodine in 0·4% KI soln. Two atoms of iodine react with one molecule of **I**. Mixtures of **I** with **II** and triethyl-lead chloride (**III**) are analysed by titrating the **I** with 0·01N-iodine as described above, separating the CCl_4 layer, which now contains triethyl-lead iodide together with **II** and **III**, and treating with $AgNO_3$, which precipitates silver from **II**, and AgI and AgCl from triethyl-lead iodide and **III**. The precipitate is filtered off and dissolved in HNO_3 and the Ag is determined by Volhard's method. The CCl_4 now contains triethyl-lead nitrate equivalent to the **I**, **II** and **III** originally present. This is converted into $PbCl_2$ by treatment with gaseous HCl (Calingaert and Cambrill, *Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 324) and the $PbCl_2$ is determined as chromate or polarographically. In mixtures containing $\simeq$ 100 mg of a mixture of the three compounds, in approx. equal proportions, the error was $\simeq$ 1%. All operations must be carried out in an atmosphere of N. J. I. M. JONES

2496. **Quantitative analysis of mixtures of benzene and isopropylbenzenes by Raman spectroscopy.** D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1634–1638.—The Raman spectra of benzene, isopropylbenzene, di-isopropylbenzenes, 1,2,4- and 1,3,5-tri-isopropylbenzenes, 1,2,4,5-tetraisopropylbenzene, ethylbenzene and 1,3,5-triethylbenzene have been recorded with a Cary Model 81 spectrometer. Synthetic eight-component mixtures of benzene and isopropylbenzenes can be analysed with an accuracy of $\simeq$ 1% (absolute). The accuracy attained compares favourably with that generally attained by i.r. methods, although this particular mixture could not have been analysed by using i.r. absorption spectra. R. M. ROWLEY

2497. **Determination of butylbenzenes.** D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1723.—Infra-red absorbancies are given for the t-, iso- and n-isomers.

2498. **Determination of ethyldimethylbenzenes.** D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1723.—Infra-red absorbancies are given for six isomers.

2499. **Identification of impurities in an acid-washed 1° coke-oven benzene.** C. F. Glick, A. J. Miskalis and T. Kessler (Applied Res. Lab., U.S. Steel Corp., Monroeville, Pa.). *Anal. Chem.*, 1960, **32** (12), 1692–1695.—After concentration by progressive freezing, the impurities were separated by gas chromatography, a 40-ft. column at 121°, with benzylbiphenyl as stationary phase, being used. The fractions were isolated in a cold trap, and the components identified and determined by means of a mass spectrometer. The occurrence of 2,2-, 2,3-, 2,4- and 3,3-dimethylpentane, 2- and 3-methylhexane, 3-ethylpentane, *cis*- and *trans*-1,2-dimethylcyclopentane, and *trans*-1,3-dimethylcyclopentane was confirmed. *cis*-1,4-*trans*-2-Trimethylcyclopentane was identified for the first time. A number of other compounds were also identified. R. M. ROWLEY

2500. **Determination of dihydroxybenzenes.** D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1722.—Infra-red data for the three isomers are included.

2501. **Chromatography by steam-distillation. I. Apparatus and application to common phenols.** C. Dumazert and C. Ghiglione (Lab. de Chim., Fac. de Méd. et de Pharm. de Marseille, France). *Bull. Soc. Chim. France*, 1960, (10), 1770–1773.—The separation of phenol, *o*-, *m*- and *p*-cresol, 2,4-xylenol, thymol, carvacrol, guaiacol and eugenol has been achieved by chromatography with steam on a column of firebrick, with silicone grease as stationary phase. The apparatus is described and illustrated. E. G. CUMMINS

2502. **The infra-red spectra of alkylphenols.** D. D. Shrewsbury (Midland Tar Distillers Ltd., Four Ashes, Wolverhampton, England). *Spectrochim. Acta*, 1960, **16** (11–12), 1294–1311 (in English).—Bar-type spectra of 111 alkylphenols in the region 650 to 1400 cm^{-1} are presented and summarised in chart form as an introduction to a more complete study. Few exceptions to the Colthup assignments (*cf. J. Opt. Soc. Amer.*, 1950, **40**, 397) in the 900 to 650-cm^{-1} region are reported, but it is shown that further characterisation is possible within the 1076 to 1329-cm^{-1} region. E. G. CUMMINS

2503. **Quantitative analysis of technical xylenols by gas chromatography and ultra-violet absorption spectrophotometry.** M. J. Bastin-Merkeman and H. G. Dietz (Lab. de Rech. Phys., Ateliers de Constructions Électriques, Charleroi, Belgium). *Chim. Anal.*, 1960, **42** (10), 493–497.—Retention times at 160° and 180°, relative to that of cyclohexanone, are given for phenol, cresols, *m*- plus *p*-ethylphenol, and xylenols, on columns containing Dow Corning Silicone 550, Apiezon L and picein as stationary phases. With a composite column (5 metres of Silicone 550, 4 metres of Apiezon L and 1 metre of picein, 20% on Johns Manville C22 firebrick) at 180° it was possible to separate and determine phenol, *o*-cresol, *m*- plus *p*-cresol, 2,6-xylenol, 2,4- plus 2,5-xylenol, *m*- plus *p*-ethylphenol, 3,5-xylenol, 2,3-xylenol and 3,4-xylenol. The ratio of *m*- to *p*-cresol was found by isolating the fraction in a cold trap, dissolving it in cyclohexane, and measuring the extinctions of the soln. at 272·5 and 286 mμ. The ratio of 2,4- to 2,5-xylenol was found in the same way by measurements at 281·5 and 285·5 mμ. The coeff. of variation was $\gtrsim$ 5%, except for ethylphenols and 3,5-xylenol, for which it was $\simeq$ 10%. R. M. ROWLEY

2504. **A precisely defined diazo coupling reagent, 5-nitrosamino-3-phenyl-1,2,4-thiadiazole (phenitrazole).** M. Pesez, J. Bartos and J.-F. Burtin (Centre de Rech., Roussel-Uclaf, Paris, France). *Talanta*, 1960, **5** (3–4), 213–215 (in French).—In acid soln. the reagent is dehydrated to the corresponding diazonium compound, which can be used

for the colorimetric determination of phenols, arylamines and aldehydes. *Procedures*—(*a*) *Phenols and arylamines*—To the ethanolic sample soln. (1 ml) add a 0·4% soln. of the reagent in ethanol (1 ml) and $HClO_4$ (55° Bé) (1 ml). Set the mixture aside for 5 min., cool in ice and add cold 20% NaOH soln. (3 ml). Set aside for a further 5 min. at room temp. before measuring the extinction. (*b*) *Aldehydes*—To the ethanolic sample soln. (1 ml) add 0·5% phenylhydrazine hydrochloride soln. (0·5 ml) and set aside for 20 min. Cool to 0°, add 1 ml of a mixture of equal vol. of $HClO_4$ (55° Bé) and a 0·4% soln. of the reagent at 0°. Set aside for 5 min. at 0°, add 20% NaOH soln. (3 ml) and measure the extinction after a further 5 min. at room temp. Carbazole and indole give positive reactions, but histidine, histamine, theophylline, caffeine, adenine, thymine and guanine, which condense with ordinary diazonium salts, do not react. Amounts of compounds required to give an extinction of 0·3 in a 1-cm cell are tabulated; these range from as little as 4 μg for phenol, and 3 μg for formaldehyde, to 65 μg for quinol and 105 μg for propionaldehyde.

W. T. CARTER

2505. **Fluorimetric determination of phthalic acid.** G. A. Thommes and E. Leininger (Kedzie Chem. Lab., Michigan State Univ., East Lansing, Mich., U.S.A.). *Talanta*, 1960, **5** (3–4), 260–263 (in English).—The phthalic acid is converted into fluorescein by treatment with conc. H_2SO_4 and resorcinol. The background fluorescence produced by the side reaction between conc. H_2SO_4 and resorcinol is minimised by measuring the fluorescence in 2N-NaOH soln. *Procedure*—To the sample soln. (1 ml) containing 0·05 to 5 mg of phthalic acid add conc. H_2SO_4 (0·04 ml) and resorcinol (5 to 10 mg). Mix and heat at 125° for 1·5 hr. Cool, dissolve the residue in water and dilute to 200 ml. Dilute a 10-ml aliquot to 100 ml with 2N-NaOH and measure the fluorescence with a fluorimeter. The accuracy is $\pm$ 5% and is not affected by the presence of up to 1 mg of iso- and tere-phthalic acids, benzoic acid or 1,4-naphthaquinone.

W. T. CARTER

2506. **Identification of organic compounds. XXXVIII. Identification of primary aromatic amines after conversion into arylazo-2-naphthols.** J. Gasparič, M. Novotná and M. Jureček (Res. Inst. for Organic Syntheses, Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (11), 2757–2764 (in German).—The aromatic amine is diazotised and coupled at a controlled pH with 2-naphthol. The product is readily identified on the micro-scale by paper chromatography or on a larger scale (after purification by column chromatography) by m.p. determination. The m.p., and R_F values in five solvent systems, of the derivatives of 35 aromatic amines are tabulated. For a polar stationary phase the R_F values are influenced by substitution by halogens in the position *ortho* to the amino-group, decreasing for the halogenoanilines in the order Cl, Br, I.

J. P. STERN

2507. **Determination of *N*-ethylaniline in *N*-ethyl-*N*-(2-hydroxyethyl)aniline.** K. B. Whetsel, W. E. Roberson and M. W. Krell (Tennessee Eastman Co., Kingsport, Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1723.—Infra-red data have been determined (*cf. Ibid.*, 1952, **29**, 1006).

2508. **Spectrophotometric determination of Flexzone 3C [*N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine] and other *p*-phenylenediamine derivatives.** C. L. Hilton (Res. Center, U.S. Rubber Co., Wayne, N.J.). *Anal. Chem.*, 1960, **32** (12), 1554–1557.—The oxidation of *p*-phenylenediamine and its derivatives to the coloured Würster salts can be carried out with cupric acetate in ethanolic soln. containing KCl and HCl. The absorption spectra of the Würster salts of a number of commercial rubber anti-ozonants, and procedures for the determination of the latter compounds, are given. If the anti-ozonant is not known, the absorption spectrum of its Würster salt can assist in its identification. Dithiocarbamate or thiuram sulphide accelerators form coloured compounds with Cu^{2+}, but other ingredients in compounded rubbers do not interfere.

R. M. ROWLEY

2509. **Chromatographic separation of a mixture of nitrobenzene with other products.** V. P. Shmonina, R. N. Khasanova and D. V. Sokol'skiĭ. *Trudy Inst. Khim. Nauk., Akad. Nauk KazSSR*, 1959, **5**, 28–35; *Ref. Zhur., Khim.*, 1960, (19), Abstr. No. 77,159.—Adsorption chromatography on Al_2O_3 (calcined for 10 hr.), moistened with rhodamine 6G (C.I. Basic Red 1) soln. and dried at 150°, can be used for the separation of a mixture of nitrobenzene (**I**), nitrosobenzene (**II**), phenylhydroxylamine (**III**), azobenzene (**IV**), hydrazobenzene (**V**), and aniline (**VI**). Observation of the separation is visual [*Ref. Zhur., Khim.*, 1956, (5), Abstr. No. 13,283]. The column is illuminated with filtered u.v. light (filter UFS–1); the zones are detected as dark bands on a fluorescing rhodamine 6G background. The test mixture is added to the column (15 mm × 200 mm), which is washed with 1% acetone in light petroleum, and the upper zone, containing **VI**, is separated. The remaining components are eluted as two fractions and chromatographed a second time. The first fraction is revealed on the column (8 mm × 200 mm) with the same reagent: **V** is eluted first, and then **IV**. The second fraction is chromatographed with 3% ether soln. in light petroleum and **I**, **III** and **II** are successively eluted. Silica gel, $Mg(OH)_2$, normal and basic magnesium carbonate, $Ca(OH)_2$ and $CaCO_3$ were tested as adsorbents; none was as satisfactory as Al_2O_3. Silica gel and $Mg(OH)_2$, activated by HCl in the cold, give good separation of the mixture, but desorption of the separated substances is extremely slow. Separated substances are identified polarographically.

K. R. COOK

2510. **Spectrophotometric determination of biphenyl in phenyltrichlorosilane and its hydrolysis products.** K. K. Popkov and S. L. Lel'chuk. USSR Pat. 129,385 (15.6.1960).—The extinctions of pure $C_6H_5SiCl_3$ and the sample are measured at 251 mμ in chloroform - ethanol (1:1); the difference is related to the content of biphenyl (**I**), which absorbs 60 times as strongly as $C_6H_5SiCl_3$ at that wavelength; 0·05 to 10·0% of **I** may be determined. A calibration curve is used to find the content of **I** from the difference in the extinctions.

C. D. KOPKIN

2511. **Colorimetric determination of triphenyltin residues.** H. J. Hardon, H. Brunink and E. W. van der Pol (Keuringsdienst van Waren, Keizersgracht 732–734, Amsterdam, Netherlands). *Analyst*, 1960, **85**, 847–849.—The sample of plant material (150 g) is extracted with 300 ml of

dichloromethane. The solvent is removed by evaporation from an aliquot (10 to 50 ml) of the extract, the residue is dissolved in $CHCl_3$ (6 ml) and the soln. is dried over Na_2SO_4. An alumina column (0·5 g in a tube 5 mm in diam.) is prepared in $CHCl_3$ and the test soln. is applied to the column immediately after the layer above the column has disappeared. The first 1-ml portion of eluate is discarded and to the next 3 ml are added 5 ml of buffer soln. (pH 8·4) then 2 ml of dithizone soln. (0·004% w/v) in $CHCl_3$. After shaking the mixture, the organic layer is separated and its extinction is measured at 610 mμ and referred to a calibration graph. Chlorophyll may interfere, but it can be removed by placing a small amount of infusorial earth on the top of the alumina. Recovery of known amounts of triphenyltin ranged from 88 to 102%. A. O. JONES

2512. **Quantitative determination of heterocyclic compounds by the use of ion-exchange paper.** A. Lewandowski and H. Wierzbicka (Chem. Inst., Univ. Poznań, Poland). *Z. anal. Chem.*, 1960, **177** (5), 334–338 (in German).—A mixture of simple heterocyclic compounds (*e.g.*, pyridine, α- and γ-picoline, 2,4-lutidine, α-collidine, piperidine, quinoline and 8-hydroxyquinoline) in 0·8 ml of water is applied to paper strips [10 mm in width and impregnated with 10% sulphophenol-formaldehyde resin (H^+ form)] and developed by the ascending technique. The ions of the base react with the resin and form corresponding zones. The areas are proportional to the amount of compound adsorbed. These zones are located with Congo red or modified Dragendorff reagent, and measured planimetrically against a standard. B. B. BAUMINGER

2513. **Infra-red spectra of heterocyclic compounds. IX. Infra-red spectra of monosubstituted quinolines and their *N*-oxides.** H. Shindo (Takamine Res. Lab., Sankyo Co., Nishi-shinagawa, Shinagawa-ku, Tokyo). *Chem. Pharm. Bull., Japan*, 1960, **8** (10), 845–855.—Details of the i.r. spectra of 20 monosubstituted quinolines, quinoline 1-oxides, and isoquinoline 2-oxides and of 18 monosubstituted quinoline 1-oxides are given. N. E.

2514. **Colorimetric methods for the determination of 2-chloro-4,6-di(ethylamino)-1,3,5-triazine (simazine) and related compounds.** M. T. H. Ragab. *Dissert. Abstr.*, 1960, **20** (12), 4507–4508.—Simazine reacted with pyridine in the presence of alkali to give a rapidly fading yellow colour, which was measured at 436·5 mμ. The addition of ethyl cyanoacetate to the soln. as soon as the yellow colour was formed produced a more stable pink colour, measured at 550 mμ. The destruction of the yellow colour with acetic acid, followed by the addition of barbituric acid, produced a reddish-violet colour, measured at 582 mμ; 2-thiobarbituric acid produced a blue colour, measured at 625 mμ. Saturation of the pyridine with glycine enhanced the colour in all four procedures. M. D. ANDERSON

2515. **Gas-chromatographic determination of traces of dissolved oxygen in motor spirit.** I. Halász and W. Schneider (Scholven-Chem. A.-G., Gelsenkirschner-Buer, Germany). *BrennstChemie*, 1960, **41** (8), 225–229.—The O in petrol is separated and determined on columns of activated carbon in copper or stainless-steel tubes of 4 mm bore, the carrier gas being electrolytic H purified by cooling with liquid N at 1 to 2 atm. To avoid loss or gain of O during sampling, a tap system, with a special lubricant, that can be swept out with H and will deliver an exact volume (≃ 2 ml) of gas or liquid is described, and the sample is drawn from a pipeline by running ≯ 2 litres of petrol through a copper tube (8 metres × 4 mm) bent into a cylindrical spiral, with a needle valve at each end; on closing the valves a sample of ≃ 100 ml is isolated without contact with air or other gas. Attached to one valve is a screw connection to a sorting column of activated carbon to retain hydrocarbons, whence a similar connection leads to the separating column of mol. sieve C (13 A) at 30°. The tap system is first filled with O, and the area of the resulting peak is compared with that from the same volume of petrol. Special thermostatic arrangements for the separating column and conductivity cell are described. All electrical and volume-measuring or regulating instruments are connected before the inlet to the column. Provided that a length of the sample ≮ 2 metres remained in the sampling tube, the standard deviation of duplicate tests was 0·6 mg of O per kg of petrol for concn. from 7 to 88 mg per kg. A. R. PEARSON

2516. **Primary standards for titration of anionic detergents using quaternary ammonium halides.** B. Veldhuis (General Chem. Div., Allied Chemical Corp., Morristown, N.J.). *Anal. Chem.*, 1960, **32** (12), 1681–1682.—Potassium 2,4,5-trichlorobenzenesulphonate is recommended for the standardisation of quaternary ammonium salts used for the titration of anionic detergents. Directions are given for its preparation. R. M. ROWLEY

2517. **Colorimetric determination of small amounts of unsaponified fat in soap.** J. Walczyńska (Dept. Anal. Chem., Politech., Warsaw, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 663–669.—Hydroxyammonium chloride reacts with fats to form hydroxamic acid, which combines with Fe^{3+} to form a violet compound. Light petroleum is used to extract fats from alcoholic soap soln., and the fats are re-dissolved in ethanol-benzene for the hydroxylamine reaction. Details of procedure are given. Standard soln. of coconut, rape, linseed and soya oils, tallow and lard gave graphs which follow Beer's law, and show comparatively small differences between fats. The method is especially sensitive for low fat contents (0·01% to 0·1%), a relative accuracy of about 10% being obtainable. P. BRYCH

2518. **Gas-phase chromatography of terpene and hydroxyphenylpropane compounds.** E. Stahl and L. Trennheuser (Botan. Inst., Univ. des Saarlandes, Saarbrücken). *Arch. Pharm., Berlin*, 1960, **293** (9), 826–837.—Mixtures of terpenes and other substances in volatile oils were separated on columns of Celite with polyoxypropylene glycol or Apiezon wax as stationary phase and He as carrier gas. Terpenes detected were camphene, α- and β-pinene, phellandrene, limonene, cineole, β-myrcene, *p*-cymene, and *trans-cis* and *trans-trans*-allo-ocimene. Camphor, eugenol (**I**), *cis*- and *trans*-iso-**I** and their methyl ethers, **I** acetate, *cis*- and *trans*-isoasaron, safrole, *cis*- and *trans*-isosafrole and β-caryophyllene were also separated. Limonene-cineole, **I**, **I** acetate and β-caryophyllene fractions were further separated by thin-film chromatography. A. G. COOPER

2519. **Determination of geraniol content of citronella oil.** F. H. L van Os and J. Sissing (Rijksuniv., Groningen, Netherlands). *Pharm. Weekbl.*, 1960, **95** (21), 686–690.—Citronellal interferes in the determination of alcohols in citronella oil since it gives a diacetate by reaction with H_2O and acetic acid during acetylation of the alcohols. It is possible to diminish this reaction by using a mixture of acetic anhydride and pyridine for acetylation. By the procedure developed, results for alcohols will be 1·7% high. The coeff. of variation of a single result (55 determinations) is 0·43%. *Procedure*—Weigh 1 g of sample, dried with anhyd. $MgSO_4$, add 2 ml of a mixture of acetic anhydride and pyridine (1:3) and heat under reflux on a boiling-water bath for 1 hr. Add 40 ml of H_2O through the condenser and heat for 15 min. Cool to room temp. and titrate with 0·5N-ethanolic KOH, with phenolphthalein as indicator. Carry out a blank similarly. M. J. MAURICE

2520. **Determination of geraniol and citronellol in geranium and citronella oils.** F. H. L. van Os and E. T. Elema (Lab. Pharmacog. Gal. Pharm., Rijksuniv., Groningen, Netherlands). *Pharm. Weekbl.*, 1960, **95** (23), 761–769.—Cold formylation cannot be used for the determination of citronellol in the presence of geraniol, since geraniol also gives a formate. This interference can be eliminated by dehydrating geraniol. Citronellol can then be determined by acetylation in pyridine soln. (*cf.* van Os and Sissing, *Anal. Abstr.*, 1961, **8**, 2519). The sum of citronellol and geraniol is determined by acetylation of the mixture, and geraniol is calculated as the difference between the results of the two determinations. The results of the determination of the total alcohol content in natural oils are low owing to the presence of linalol, which is only 5% acetylated with acetic anhydride and pyridine. *Procedure for the dehydration of geraniol*—Add 0·2 g of toluene-*p*-sulphonic acid and 12 to 18 g of xylene to 8 to 12 g of the oil in a round-bottomed flask, which is fitted with a condenser containing a vertical side-tube. Heat for 30 min.; the azeotropic mixture distils off and the water separates in the side-tube while the xylene runs back to the flask. Cool and wash the mixture with 10% NaCl soln. (3 × 50 ml). Dry the xylene soln. with anhyd. $MgSO_4$ and determine citronellol by acetylation. M. J. MAURICE

2521. **Determination of citronellol by formylation.** F. H. L. van Os and G. D. de Boer (Rijksuniv., Groningen, Netherlands). *Pharm. Weekbl.*, 1960, **95** (22), 735–738.—Two methods for the determination of citronellol are examined, with citronellol of 96·7% and 99·7% purity. It is found that cold formylation according to the method of ISO/TC 54-249 yields accurate results. Hot formylation as described in ISO/TC 54-248 yields results that are 6 to 11% high. M. J. MAURICE

2522. **The action of hydrogen peroxide and sulphuric acid mixtures and their application to the analysis of explosives.** M. Parpaillon and S. Rigal. *Mém. Poudres*, 1960, **42**, 285–295.—The use of hydrogen peroxide - sulphuric acid mixtures and their application to the determination of carbon black and cryolites in explosives is discussed. The sample (≃ 5 g) is thoroughly wetted with 15 ml of conc. H_2SO_4 and 2 drops of 110-vol. H_2O_2 are added. When the initial reaction has subsided, 25 ml of 110-vol. H_2O_2 is added in small amounts; the pale-yellow soln. produced is decolorised by gentle warming. Carbon black and similar substances are determined by filtering the soln. on a tared sintered-glass crucible, washing the residue with boiling ammonium acetate soln. (ammonium acetate 500 g, acetic acid 40 ml, and H_2O 500 ml), then with H_2O, ethanol and acetone, and drying at 130°. Cryolite ($3NaF.AlF_3$) or potassium cryolite ($3KF.AlF_3$) can be calculated from the determination of Al in the filtrate, gravimetrically as the 8-hydroxyquinolinate. The relative error for carbon black varies from 0·01 to 0·05%, while that for cryolites is ± 2%. R. A. HENDEY

2523. **Activation analysis of mercury in cellulose products.** T. Westermark, B. Sjøstrand and P. O. Bethge (Royal Inst. of Technol., Stockholm 70, Sweden). *Svensk Papp-Tidn.*, 1960, **63** (8), 258–263 (in English).—By using neutron activation in a reactor, it is possible to determine Hg in microgram quantities. The content of Hg in mechanical pulp can be determined easily as well as the content in paper resulting from the control of the slime in paper mills. Comparisons are made with other methods and the relative merits of different methods, including the gas-spectrophotometric one, are discussed. Activation analysis can always serve as a standard method whenever comparisons are of interest. The special case of Hg in corroded aluminium seems to be a favourable one for the activation method. P. PEDERSEN

2524. **Modified method for determination of active agent and degree of substitution in carboxymethylcellulose (CMC).** K. Wilson (Cellulose Res. Lab., Uddeholms AB, Skoghallsverken, Skoghall, Sweden). *Svensk Papp-Tidn.*, 1960, **63** (20), 714–715 (in English).—A previously described method (*Ibid.*, 1956, **59**, 218) has given erroneous results for CMC grades with a degree of substitution above 0·8. The method has been changed, retaining the acid treatment as before, but neutralising the acid with an aq. soln. of NaOH instead of an ethanolic soln. of NaOH. Pure sodium CMC is then quant. pptd. by addition of ethanol. Reproducible figures are then obtained for both active agent and degree of substitution. P. PEDERSEN

2525. **Analysis of cellulose acetobutyrate.** U. Bartels and H. Hoyme (Inst. f. Faserstoff-forsch., Teltow-Seehof, Deutsch. Akad. Wiss., Berlin). *Faserforsch. u. Textiltech.*, 1960, **11** (10), 503–505.—An improved and accurate method is devised for determining the acetic (**I**) and butyric (**II**) acid contents of cellulose acetobutyrate based on determinations of **I** plus **II** by saponification and of **II** by oxidation with $K_2Cr_2O_7$ - H_2SO_4. *Procedure*—The powdered sample (0·5 g) is saponified with 15 ml of 0·5N-ethanolic KOH for 72 hr. at 20° or 15 hr. at 40°; the resulting soln. is diluted and filtered from the regenerated cellulose; the filtrate plus washings are made up to 100 ml, and 10-ml aliquots are taken for the determinations. The first aliquot is steam-distilled with 1 ml of H_3PO_4 (sp. gr. 1·7), and the distillate is titrated for the liberated **I** plus **II** with 0·1N-ethanolic KOH to phenolphthalein. The second aliquot is evaporated to dryness and, after adding 10 ml of water, again evaporated (this procedure is essential for accuracy); the cooled residue is mixed with 15 ml of 0·25N-$K_2Cr_2O_7$ and 10 ml of conc. H_2SO_4, with cooling (the $K_2Cr_2O_7$ to acid ratio is critical), and the mixture is heated under reflux for 1 hr., and then made up

to 100 ml. To a 25-ml aliquot is added 10 ml of 10% KI soln. and the liberated iodine is titrated with 0·1N-$Na_2S_2O_3$ to give the content of **II**; **I** is obtained by difference. H. L. WHITEHEAD

2526. **Improvements in the determination of the degree of polymerisation of cellulose by the nitrate method.** V. Mašura (Dept. Cellulose, Chem. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (10), 707–716.—The accuracy and reliability of the nitrate method (Alexander and Mitchell, *Anal. Chem.*, 1949, **21**, 1497) were increased by modifying the preparation of the nitration mixture, the nitration procedure, the stabilisation of the cellulose nitrate formed, its dissolution, its pptn. with acetone and the measurement of the viscosity. J. ZÝKA

2527. **Determination of the concentration of poly(butyl methacrylate) in monomer.** V. Šraier (Inst. Nuclear Res., Czech. Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (11), 2922 (in German).—The sample (containing 0·05 to 0·2 g of polymer) is freed from monomer by repeated vacuum-evaporation with acetone (10 to 20 ml) at 40°; the residual film is dried to constant weight at 120°. The reproducibility of the method is within ± 2·5%. The polymer finally obtained is not representative of that originally present.
J. P. STERN

2528. **The dye-partition test for detecting carboxyl, sulphate and hydroxyl end-groups in high polymers.** S. R. Palit. *Makromol. Chem.*, 1960, **38**, 96–104.—The distribution of a cationic dye between water and an organic solvent, when the dye and the polymer are soluble in only the water and the organic solvent, respectively, can be used for determining the acid groups in the polymer. If the polymer contains anionic groups, coloration of the non-aq. layer takes place. Accurate conditions are specified for carrying out the test to determine strong acid groups (*e.g.*, $-SO_3H$ and $-SO_4H$) and carboxyl groups. A slightly modified test can be used for detecting hydroxyl groups. Some examples are given as illustration.
BRIT. COTT. IND. RES. ASS. ABSTR.

2529. **Spectrophotometric determination of sulphide end-groups and number-average molecular weight in high polymers.** I. Rosenthal, G. J. Frisone and J. K. Coberg (Res. Lab., Rohm & Haas Co., Philadelphia, Pa.). *Anal. Chem.*, 1960, **32** (12), 1713–1716.—The complex formed between iodine and sulphide end-groups absorbs strongly in the u.v., with a maximum at 308 mμ in dichloromethane soln. If the end-group is known, the number-average molecular weight (M) of the polymer can be calculated from the equation $M = \epsilon c/A$, where ϵ = molar absorptivity of a mercaptan dimer having the same end-group, c = concn. of polymer (g per litre), and A = extinction of polymer. If the end-group is not known, it can be identified by means of the molecular extinction coeff., if the number-average molecular weight is known. Determinations were made on poly(methyl methacrylate) samples prepared by free-radical polymerisation with each of three mercaptans as chain-transfer agents. Good agreement was attained between molecular weights obtained by this spectrophotometric method and by osmotic-pressure measurements. The coeff. of variation of nine results obtained on different days was ≃ 10%.
R. M. ROWLEY

2530. **Dynamic mechanical spectrometry [of polymers] by means of rolling-friction measurements.** D. G. Flom (General Electric Res. Lab., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1550–1554.—Measurements of the values of rolling friction for polymers over the range of temperature from − 40° to 300° have shown that the results obtained can be correlated with those in the published work on the determination of dynamic mechanical loss as a function of stress frequency. Application of these measurements to the problems of differentiation between polymers, determination of the extent of chain branchings, the degree of crystallinity, the concn. of plasticiser and the detection of individual components in polymer blends is discussed. E. G. CUMMINS

2531. **Polymer wedge for the infra-red determination of methyl groups in polyethylene.** M. C. Harvey and L. L. Peters (W. R. Grace & Co., Clarksville, Md., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1725.—The preparation of a compensating wedge from a high-mol.-wt. polyethylene that contains ≃ 1 methyl group per mol. is described. A wedge of this type can be used in a double-beam technique to compensate for the 1367-cm^{-1} (7·31 μ) methylene band, leaving the 1378-cm^{-1} (7·25 μ) methyl band to stand alone. E. G. CUMMINS

2532. **Estimation of hydroxyl, methyl and phenyl in dimethyldiphenyl silicone resins by infra-red spectrophotometry.** E. R. Shull (Linde Co., Div. of Union Carbide Corp., Tanawanda, N.Y.). *Anal. Chem.*, 1960, **32** (12), 1627–1630.—A film of the resin is formed on a sodium chloride plate by evaporating a toluene soln.; if the resin is insoluble it is either dispersed in KBr and a disc is pressed, or it is mulled with a fluorolube oil. The i.r. spectrum from 2 to 4 μ is obtained, and the base line is drawn between the points of highest transmission in the region of 2·5 μ to 3·9 μ. The relative extinctions of the peaks at 2·8 μ, 2·9 μ, 3·3 μ and 3·4 μ are measured. The methyl and phenyl contents are found by calculating $D_{3\cdot3}/D_{3\cdot4}$ (D = extinction) and referring to the curves of methyl content and phenyl content *vs.* $D_{2\cdot3}/D_{3\cdot4}$ obtained by measurements on resins of known composition. The free and hydrogen-bonded hydroxyl contents, relative to the methyl content, are proportional to $D_{3\cdot8}/D_{3\cdot4}$ and $D_{2\cdot8}/D_{3\cdot4}$; the constants are calculated from measurements on resins of known composition. The method is suitable for resins containing up to 25% of total hydroxyl groups, 7 to 21% of methyl groups and 18 to 56% of phenyl groups.
R. M. ROWLEY

2533. **Chromatographic micro-determination of zinc in natural and synthetic rubbers.** M. Piazzi (Siena Univ., Italy). *Ann. Chim., Roma*, 1960, **50** (8–9), 1176–1180.—The org. matter is destroyed by treatment with fuming HNO_3 - $HClO_4$ and the residue is dissolved in HCl. The soln. is applied to filter-paper and submitted to radial chromatography, with n-butanol - ethyl acetate - HCl (*d* 1·18) (9:9:2). The Zn is made visible with dithizone and its concn. determined from the height of the band. Other elements (*e.g.*, Fe, Cu, Mn, Co, Ni and Se) do not interfere. L. A. O'NEILL

2534. **Determination of nitrogen with titanous salts. Application to propellent powders and their constituents.** L. Marvillet and J. Tranchant. *Mém. Poudres*, 1960, **42**, 271–284.—Titanous and ferrous salts are used for the determination of nitric esters, nitro-derivatives and cellulose nitrate (**I**) in

explosives. *Procedures*: (*i*) *For nitric esters other than* **I**—Dissolve the sample (≃ 1 g) in glacial acetic acid and make up to 250 ml. Transfer 25 ml to a 250-ml flask fitted with a side arm, add 15 ml of 0·7N-$FeCl_2$ (200 g of $FeCl_2.4H_2O$ and 50 ml of conc. HCl diluted to 1 litre with H_2O, then heated with 5 to 10 g of iron powder for 15 min. and filtered) and 25 ml of HCl (1:1), and boil under reflux for 5 min., passing CO_2 continuously, then cool and titrate the $FeCl_2$ formed with 0·2N-$TiCl_3$. (*ii*) *For nitro-derivatives*—Prepare the sample soln. as for (*i*), and transfer 25 ml to the reaction flask. Add 50 ml of 0·2N-$TiCl_3$ and heat under reflux for 5 min., passing CO_2 continuously. Cool and titrate the excess of $TiCl_3$ with 0·15N-$(NH_4)_2SO_4.Fe_2(SO_4)_3$. (*iii*) *For mixtures of nitric esters and nitro-derivatives*—Determine the nitric esters as described under (*i*), then add to the same soln. 50 ml of 0·2N-$TiCl_3$, heat under reflux for 5 min., passing CO_2 continuously. Cool and titrate the excess of $TiCl_3$ with 0·15N-$(NH_4)_2SO_4.Fe_2(SO_4)_3$. (*iv*) *For* **I**—Dissolve the sample (0·8 to 1 g) in 250 ml of glacial acetic acid - butyl acetate (1:1). Transfer 25 ml to the reaction flask, add 25 ml of 0·7N-$FeCl_2$ and 25 ml of HCl (1:1), and heat under reflux for 3 to 4 hr., passing CO_2 continuously. Cool, and titrate with 0·1N-$TiCl_3$. Results for nitric esters, **I** and most nitro-derivatives are accurate to within 1 to 2%, and compare well with those by Devarda's method. Trinitrotoluene gives a constant recovery of 94%, and a factor is therefore used.

R. A. HENDEY

2535. **Application of the cathode-ray polarograph to the analysis of explosives. III. Simultaneous determination of nitroglycerin and dinitroglycol [ethylene dinitrate.]** J. S. Hetman (Southern Instruments Ltd., Camberley, Surrey, England). *Talanta*, 1960, **5** (3–4), 267–271 (in English).—Nitroglycerin (**I**) and ethylene dinitrate (**II**) are both reduced at the dropping mercury electrode in a base electrolyte containing N-KCl (10 ml), 2N-NH_4Cl (50 ml) and H_2O (40 ml). **I** gives three waves at − 0·35 V, − 0·44 V and − 0·62 V, and **II** gives two waves at − 0·44 V and − 0·62 V, *vs.* the mercury pool. Blasting explosives containing ≃ 10% of **I** and 3% of **II** gave results with an accuracy within ≃ 3%. If 10% (v/v) of pyridine is added to the base electrolyte, **I** gives a single wave at − 0·27 V and **II** is not reduced at all, indicating the possibility of determining **I** in the presence of an excess of **II**. W. T. CARTER

2536. **Chromatographic analysis of explosives. Quantitative analysis of phthalic esters.** L. Marvillet. *Mém. Poudres*, 1960, **42**, 247–260.—The determination, in mixtures of explosives, of diethyl (**I**), dibutyl (**II**) and dioctyl (**III**) phthalates is studied on a column of Levilite - Celite 535 (3:1), activated overnight at 120°. Details of the solvents and developers (light petroleum, ethyl ether and benzene mixtures) are given for the separation of **I**, **II** and **III** from centralite, nitroglycerin, diphenylamine and mixtures of explosives. After separation, the phthalates are dissolved in ethanol, and the extinctions are read at 275 mμ. Errors of up to 6% can be expected, owing to the non-reproducibility of the columns, and to the small quantities employed (10 to 20 mg).

R. A. HENDEY

2537. **Simultaneous polarographic determination of pentaerythritol tetranitrate and cyclotrimethylenetrinitramine.** J. S. Hetman (Southern Instruments Ltd., Frimley Road, Camberley, Surrey, England). *Anal. Chem.*, 1960, **32** (12), 1699–1701.—The method is suitable for the determination of pentaerythritol tetranitrate (**I**) and cyclotrimethylenetrinitramine (**II**) within 20 min. with an accuracy of ± 1%. *Procedure*—Dissolve the sample, containing about 30 mg each of **I** and **II**, in pyridine (5 ml) at 50° or 60°, cool, and dilute to 20 ml with ethanol. Dilute a 0·5-ml aliquot to 10 ml with base electrolyte [mix pyridine (30 ml) with M-KNO_3 (7 ml), 2M-NH_4NO_3 (35 ml) and H_2O (28 ml)]. De-aerate and record polarograms starting at − 0·05 V and − 0·65 V *vs.* the mercury-pool reference electrode. Cellulose nitrate, perchlorates, 2-nitrodiphenylamine, *m*-nitrotoluene and ethylene dinitrate do not interfere. Nitroglycerin (**III**) and pentaerythritol trinitrate interfere with the determination of **I**; dinitrotoluene interferes with the determination of **II**; trinitrotoluene interferes with the determination of both **I** and **II**. To determine **I** in the presence of **III**, apply a correction for the amount of **III** determined as follows. Mix the sample soln. (1 ml) with pyridine (0·5 ml), dilute to 10 ml with electrolyte soln. [mix M-KCl (10 ml) with 2M-NH_4Cl (50 ml) and H_2O (40 ml)], shake, filter through paper and record the polarogram from − 0·05 V. A. R. ROGERS

See also Abstracts—**2274**, Chemiluminescent indicators for weak acids. **2338**, Org. C in geochemical analysis. **2365**, Mass spectrometry of hydrocarbons. **2369**, P in coal. **2602**, Determination of aniline, pyridine deriv., etc. **2661**, Nitrobenzene in air. **2691**, Chromatography of sugars.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

2538. **Simple wet-oxidation procedure for biological materials.** L. L. Reitz, W. H. Smith and M. P. Plumlee (Animal Sci. Dept., Purdue Univ., West Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1728.—Digest the sample (5 g) for 4 to 6 hr. at a low temp. with conc. HNO_3 (35 ml) and cool overnight. If a solid fat separates, filter through glass wool, wash the filter with conc. HNO_3 and add the washings to the filtrate. Add conc. H_2SO_4 (2 ml), heat rapidly until charring occurs and add dropwise 72% $HClO_4$ - conc. HNO_3 (2:1) (0·5 to 3 ml) until the soln. is clear and colourless. Heat to fuming for 10 to 15 min., cool, add H_2O (10 ml) and conc. HCl (3 ml) and boil until dissolution is complete. The method is safe; it needs little attention and no special equipment. A. R. ROGERS

2539. **A technique of blood-pH estimation.** E. G. Hardy (Dept. of Surgery, Univ. Durham, England). *J. Clin. Path.*, 1960, **13** (2), 173–174.—A length of 1-mm-bore glass capillary-tubing in the shape of a flattened U has two small chambers with lateral ports, arranged so that a glass electrode and an electrolyte junction to a calomel half-cell can be fitted by means of P.V.C. sleeves. The assembly is supported in a water bath at a constant temp. A polyethylene tube of 1-mm bore connects the

apparatus to a manifold constructed of two three-way adapters attached to two 10-ml syringes. The apparatus is filled with heparinised saline which, in use, is drawn into one syringe followed by the blood sample drawn into the other syringe.

R. A. BRENAN

2540. **Clinical applications of infra-red spectroscopy. II. Identification of pathological concretions and other substances.** B. Klein, M. Weissman and J. Berkowitz (Vet. Admin. Hosp., Bronx, N.Y., U.S.A.). *Clin. Chem.*, 1960, **6** (5), 453–465.—Infra-red absorption spectra are given for typical calculi from the prostate, salivary gland and biliary tract, and for dental calculi; potassium bromide pressed-disc preparations are used for the analysis. Application to the examination of tissues and body fluids for alcohols and barbiturates is also described.

H. F. W. KIRKPATRICK

2541. **Estimation of lithium in blood.** G. R. J. Barrow (Biochem. Dept., Hellingly Hospital, Hailsham, Sussex, England). *J. Med. Lab. Technol.*, 1960, **17** (4), 236–238.—The determination of Li in a 1 in 10 dilution of heparinised plasma or whole blood with the EEL flame photometer is described. A soln. containing 1 mg of Li per 100 ml is used to set the full-scale deflection of the instrument, but the result is calculated from a calibration curve prepared by the addition of Li to normal blood to cover the range 0 to 4 mg per 100 ml. The effect of variations in the concn. of Na, K, Ca, phosphate and protein present is discussed.

R. A. BRENAN

2542. **Determination of heavy water in plasma or urine.** O. H. Gaebler and H. C. Choitz (Edsel B. Ford Inst. for Med. Res., Henry Ford Hosp., Detroit, Mich., U.S.A.). *Clin. Chem.*, 1960, **6** (6), 549–557.—A mass-spectrometric method is described.

H. F. W. KIRKPATRICK

2543. **Analysis of sodium, potassium and calcium in biological materials by the EEL flame photometer, with algebraic corrections for mutual interference effects.** I. F. Duthie and I. McDonald (Rowett Res. Inst., Bucksburn, Aberdeen, Scotland). *Lab. Practice*, 1960, **9** (10), 705–709; 732.—Regression equations are derived for the mutual interference effects of Na^+, K^+, Ca^{2+} and PO_4^{3-} in the concn. ranges normally encountered in soln. prepared from biological materials. The effect of high concn. of PO_4^{3-} on the emission of Ca^{2+} is too great for satisfactory correction, and previous removal of PO_4^{3-} by anion-exchange on Amberlite IR-45 is advocated. Full working details for the preparation of the sample soln. and for the application of the corrections are given. Corrected results for Na^+, K^+ and Ca^{2+} showed coeff. of variation of $\simeq 1\%$, and recoveries from 97 to 103%.

E. C. APLING

2544. **Determination of intracellular magnesium by an automatic titration procedure.** D. A. Sones, W. F. McGuckin and K. G. Wakim (Mayo Clinic and Mayo Found., Rochester, Minn., U.S.A.). *Clin. Chem.*, 1960, **6** (6), 564–571.—Modifications of the method of Malmstadt and Hadjiioannou (*Anal. Abstr.*, 1959, **6**, 4503) are described that allow measurement of intracellular levels.

H. F. W. KIRKPATRICK

2545. **Modified method for the determination of serum calcium in the presence of magnesium using Cal-Red indicator.** A. R. Pappenhagen and H. D. Jackson (Dept. of Biochem., Purdue Univ., Lafayette, Ind., U.S.A.). *Clin. Chem.*, 1960, **6** (6), 582–584.—To the serum (0·1 ml) add 0·8N-NaOH (0·5 ml) and 1 drop of Cal-Red indicator [3-hydroxy-4-(2-hydroxy-4-sulpho-1-naphthylazo)-2-naphthoic acid] (0·4% in 95% ethanol). Titrate within 10 min. to the blue end-point with EDTA (0·5 milliequiv. per litre). The end-point may be improved by adding a few drops of methyl red or methyl orange (4 mg per 100 ml in 95% ethanol), when the colour change is from red to blue - green.

H. F. W. KIRKPATRICK

2546. **Simple and rapid method for the simultaneous determination of calcium and magnesium from the same sample of blood serum.** G. S. Kovács and K. E. Tárnoky (Surgical Clin., Med. Univ. of Szeged, Hungary). *J. Clin. Path.*, 1960, **13** (2), 160–162.—In the titrimetric method described, disodium 1-(5-chloro-2-hydroxyphenylazo)-4,5 - dihydroxynaphthalene - 2, 7 - disulphonate (Plasmocorinth B) is used as the indicator. Serum (0·5 ml), water (5 ml), 0·5N-NaOH (1·5 ml) and 0·01% Plasmocorinth B soln. (1 ml) are placed in a 50-ml beaker and titrated with 0·001M-EDTA from a 2-ml micro-burette to a bluish-violet end-point (titre × 8 ≡ mg of Ca per 100 ml). To the same sample are added 0·5N-HCl (1·2 ml) and 0·83% NH_4Cl soln. containing 12 ml of conc. aq. NH_3 per 100 ml (1·5 ml) and the mixture is titrated to a pale-blue end-point with 0·001M-EDTA (titre × 4·86 ≡ mg of Mg per 100 ml). The recovery of added Ca ranged from 97·5 to 104·2% (average 100·4%) and of added Mg from 96·3 to 104·2% (average 101·3%). The standard deviation of 25 duplicate determinations was ± 0·23 mg of Ca per 100 ml and ± 0·20 mg of Mg per 100 ml.

R. A. BRENAN

2547. **Colorimetric determination of boron in plant material with quinalizarin.** B. Bardzicka and A. Krauze (School of Agric., Olsztyn, Poland). *Chem. Anal., Warsaw*, 1960, **5** (5), 791–795.—Ignite the powdered sample (0·5 to 2·0 g) in a quartz crucible at 450°, add satd. $Ca(OH)_2$ soln. (2 ml per g of sample) and heat at 600° for 30 min. Dissolve the ash in N-H_3PO_4 (10 ml) and filter. Evaporate 5 ml of filtrate and dry at 150° for 2 hr., dissolve in conc. H_2SO_4 (5 ml) and add a few crystals of $(NH_4)_2SO_4.FeSO_4.6H_2O$. To 1·5 ml of this soln. add 1 ml of 0·01% quinalizarin in conc. H_2SO_4, close the tube and measure the extinction at 610 mμ after 1 hr. Refer results to a calibration curve, prepared by the same procedure. The method is satisfactory for concn. up to 10 μg of B in 2·5 ml. The accuracy is ± 3·6%.

B. K.

2548. **Extraction and flame-spectrophotometric estimation of thallium in urine.** W. B. Stavinoha and J. B. Nash (Dept. of Pharmacol. and Toxicol., Univ. of Texas Med. Branch, Galveston, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1695–1697.—*Procedure*—Evaporate the sample (25 ml) to dryness with conc. HNO_3 (20 ml), add H_2O (5 ml), 48% HBr soln. (0·5 ml) and Br (0·05 ml), heat to drive off the Br, and cool. Add a satd. soln. of HBr in octan-2-one (5 ml), shake for 1 min. and allow the layers to separate. Wash the upper layer with dil. HBr soln. (5 ml) and examine in a flame

spectrophotometer at 377·6 mμ. Use a soln. containing 5 μg of Tl per ml as standard and solvent as blank. No interference is found with any of 19 elements in the amounts likely to be present in urine. The mean recovery of 12·5 μg of Tl in 18 determinations was 12·4 μg, with a standard deviation of ± 0·6 μg. A. R. ROGERS

2549. **Determination of arsenic in biological material by the arsenic mirror test.** A. Dyfverman and R. Bonnichsen (Govt. Lab. for Forensic Chem., Stockholm, Sweden). *Anal. Chim. Acta*, 1960, **23** (5), 491–500 (in English).—The arsenic mirror obtained in the Marsh - Berzelius test is dissolved in NaBrO soln. and the As is determined spectrophotometrically by a modification of the molybdenum blue method of Jacobs and Nagler (*cf. Brit. Abstr. A*, 1942, 339). The range of the method is 2 to 80 μg of As, but the yield in the arsenic mirror varies from 50 to 85% in different circumstances and calibration is consequently necessary for different types of sample. Visible and i.r. absorption spectra were determined for the blue reduction products of molybdoarsenic acid and other heteropoly-acids. The soln. of the arsenic mirror in Br soln. is submitted to paper chromatography for confirmatory identification. H. N. S.

2550. **Manometric micro-apparatus for estimating oxygen [in blood].** F. Rappaport, F. Eichhorn and M. Nutman (Weizmann Inst. of Sci., Rehovot, Israel). *J. Clin. Path.*, 1960, **13** (2), 176–178.—A procedure is given for the determination of the oxygen content of blood with the apparatus previously described (*Ibid.*, 1956, **9**, 166; *Clin. Chim. Acta*, 1956, **1**, 305). R. A. BRENAN

2551. **Radiometric determination of chlorides in plasma and blood.** A. A. Shatalova and G. I. Meerov (Psychoneurological Res. Inst., Leningrad). *Biokhimiya*, 1960, **25** (5), 769–772.—*Procedure*—Prepare two soln. containing H_2O (2 ml), conc. HNO_3 (2 ml) and freshly prepared $^{110}AgNO_3$ soln. in acetic acid (5 ml) (2300 to 2500 counts per 5 ml per min.), prepared from 0·01N-$AgNO_3$ and $^{110}AgNO_3$. To one soln. add 0·1M-NaCl (0·2 ml) and, to the other, blood or plasma (0·2 ml). Stand both soln. in a water bath (15 min. for plasma, 30 min. for blood), cool, centrifuge for 15 min. at 2500 r.p.m., pour off the supernatant liquids, wash the residues with 0·008M-HNO_3 (5 ml) and re-centrifuge. Dissolve the residues in 4% aq. NH_3 soln. (10 ml) and measure the activity of the $^{110}AgCl$ during 5 min. With special glass cells (30 mm diam.) and an MS–7 γ-counter, chlorides were determined with an accuracy of ± 8% in plasma and ± 8% in blood. K. R. COOK

2552. **Determination of serum butanol-extractable iodine with a modified alkaline incineration procedure.** D. Klein and J. M. Chernaik (Long Island Lab., Flushing, N.Y., U.S.A.). *Clin. Chem.*, 1960, **6** (5), 476–484.—Extraction of the serum (1 ml) after addition of 10% H_2SO_4 (0·1 ml) is carried out in tubes (16 mm × 125 mm) by mixing the n-butanol (3 ml) with a special stirrer (a glass rod 4 mm in diam. and 17 cm long flattened to a button 8 to 9 mm in diam. at the mixing end) intermittently for 10 min., followed by centrifuging. The butanol is decanted into a separating-funnel and two further extractions are made. The combined butanol extracts are washed with Blau reagent (3 × 5 ml) and the butanol is evaporated off in a tube. The iodine is then determined by a modification of the method of Barker *et al.* (*J. Clin. Invest.*, 1951, **30**, 55). H. F. W. KIRKPATRICK

2553. **Serum iron determination.** D'A. Kok and F. Wild (Dept. of Med., Univ. Cambridge, England). *J. Clin. Path.*, 1960, **13** (3), 241–245.—Serum (2 ml), re-distilled thioglycollic acid (2 drops), 2N-HCl (1 ml) and 40% trichloroacetic acid (0·5 ml) are stirred vigorously with a glass rod for about 45 sec. in a centrifuge tube and then centrifuged for 10 min. The supernatant liquid (2 ml), satd. Na acetate soln. (1 ml) and 0·4% ethanolic bathophenanthroline soln. (1·5 ml) are placed in a stoppered tube and mixed by swirling. Full colour development occurs within 30 sec. and the extinction is then read at 536 mμ. Iron standards containing 1 and 2 μg of Fe per 2 ml and a reagent blank (2 ml of water) are prepared in a similar manner. For values above 300 μg of Fe per 100 ml, serum (1 ml), 2N-HCl (0·5 ml), 40% trichloroacetic acid (0·25 ml), supernatant liquid (1 ml), Na acetate soln. (0·5 ml) and bathophenanthroline soln. (3 ml) are substituted for the quantities used above. The method is compared with that of Peters *et al.* (*Anal. Abstr.*, 1957, **4**, 3053). R. A. BRENAN

2554. **Determination of serum iron after the intravenous injection of iron-dextran.** D. Webster (General Hospital, Sunderland, England). *J. Clin. Path.*, 1960, **13** (3), 246–248.—A rapid method suitable for the determination of serum iron after the intravenous injection of iron-dextran in plasma-volume studies is described. The reagent is prepared by dissolving bathophenanthroline (5 mg) in Teepol concentrate (27% active ingredient) (10 ml) with gentle heating and diluting to 100 ml with water. The presence of the detergent prevents protein pptn. and renders the bathophenanthroline and its ferrous complex soluble. Serum (0·2 ml), reagent (3·8 ml) and sodium dithionite (10 to 20 mg) are mixed in a tube and placed in a water bath at 90° to 95° for 3 min. After cooling the soln., the extinction is read against a reagent blank at 530 mμ. Standards containing 15 and 30 μg of Fe per ml are treated similarly. R. A. BRENAN

2555. **Fluorescence X-ray determination of selenium in plant material.** R. Handley (Dept. of Soils and Plant Nutrit., Univ. of Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1719–1720.—The K_α peak of Se at 1·106 A has been used in the method described. The LiF analysing crystal ($2d$ = 4·0269 A) employed has provided satisfactory resolution of the Se peak from As at 1·177 A and Br at 1·041 A. When a given correction for matrix effects, dependent on the plant material, is applied, a linear relationship is obtained between corrected counts per sec. and known Se content, for the range 0 to 300 p.p.m., this ratio being ≃ 0·32. More than 20 min. per determination would be required for samples containing < 10 p.p.m. if the probable error was to be kept at < 10%. E. G. CUMMINS

2556. **Modified Cavett method for the determination of alcohol in body fluids.** L. C. Nickolls (The Metropolitan Police Lab., New Scotland Yard, London). *Analyst*, 1960, **85**, 840–842.—The Cavett

micro-method for the determination of alcohol in body fluids (Kent-Jones and Taylor, *Ibid.*, 1954, **79**, 121) is modified so as to improve its reproducibility and remove difficulties occurring when a micro-method is used in routine work with large numbers of samples. The vessel used is a squat 16-oz specimen jar with a ground top sealed by means of a ground glass plate and a screw cap. The standard $K_2Cr_2O_7$ soln. [10 ml of a 0·1N soln. in 50% (v/v) H_2SO_4] is placed in the jar in which a glass triangle supports a Petri dish containing 2 ml of the body fluid. The jar is then sealed and placed in an incubator at 37° for $\lesssim$ 8 hr. The Petri dish and triangle are removed, the triangle being rinsed into the jar, and the contents are diluted to $\simeq$ 12 oz. Solid KI (2 g) is added and the liberated iodine is titrated with 0·1N-$Na_2S_2O_3$, starch soln. being added as the end-point is approached. A blank determination is made with omission of the sample. A. O. JONES

2557. **Rapid method for determination of ascorbic acid in urine.** A. Polk, T. L. Flanagan and E. J. Van Loon (Smith, Kline and French, Philadelphia, Pa., U.S.A.). *Clin. Chem.*, 1960, **6** (6), 558–563.—Dilute the urine with 5% HPO_3 in 10% acetic acid to give a concn. of 5 to 10 μg of ascorbic acid per ml. To 2 ml add 1 drop of 0·2% aq. 2,6-dichlorophenolindophenol and 2 ml of 1% thiourea soln. in 5% HPO_3, mix and add 2,4-dinitrophenylhydrazine soln. [2% in H_2SO_4 - H_2O (1:3)] (1 ml). Place the tube in boiling water for exactly 10 min., then cool in ice. Add 5 ml of freshly mixed conc. HCl - 85% H_3PO_4 (3:2) and after 10 min. at room temp. read the extinction at 540 mμ. Treat standards containing 0 to 30 μg of ascorbic acid in 2 ml of 5% HPO_3 in 10% acetic acid in the same manner.

H. F. W. KIRKPATRICK

2558. **Nicotinic acid assay in blood and urine.** H. Baker, O. Frank, I. Pasher, S. H. Hutner and H. Sobotka (Mt. Sinai Hosp., New York, U.S.A.). *Clin. Chem.*, 1960, **6** (6), 572–577.—A specific and sensitive assay is described in which a strain of *Tetrahymena pyriformis* is used.

H. F. W. KIRKPATRICK

2559. **Determination of hydrochlorothiazide in urine.** H. Sheppard, T. F. Mowles and A. J. Plummer (Ciba Pharmaceutical Products Inc., Summit, N.J.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (11), 722–723.—Dilute the urine sample (1 ml) with H_2O (2 ml), extract with ethyl acetate (2 × 18 ml) and evaporate the combined extracts to dryness *in vacuo* at 45°. Extract the residue with acetone (5 ml), evaporate a 0·5-ml aliquot to dryness, heat with a 0·2% soln. of chromotropic acid in 15M-H_2SO_4 (1 ml) for 5 min. in a boiling-water bath, cool and measure the extinction at 570 mμ. Calculate by reference to a standard curve prepared by application of the procedure to soln. of hydrochlorothiazide (20 to 100 μg) in control urine. Alternatively, hydrolyse the residue from the ethyl acetate extraction by heating with 5N-NaOH for 30 min., acidify, diazotise, couple with *N*-1-naphthylethylenediamine and measure the colour in a Klett - Summerson colorimeter with a No. 54 filter. The two methods give essentially identical results, but the chromotropic acid method is preferred because it is not subject to interference by chlorothiazide and sulphonamides.

A. R. ROGERS

2560. **Quantitative determination of 3-methoxyadrenaline and 4-hydroxy-3-methoxymandelic acid as vanillin in human urine.** K. Ryšánek, V. Kordová and Č. Švorčík (Dept. Exp. Therapy, Prague-Krč, Czechoslovakia). *Čas. Lék. Čes.*, 1960, **99** (37), 1179–1181.—The method is based on the conversion of both 3-methoxyadrenaline and 4-hydroxy-3-methoxymandelic acid with HIO_4 into vanillin, which is separated chromatographically from impurities and quant. evaluated in u.v. light. *Procedure*—Adjust the urine sample (20 ml) to pH 1 with HCl and hydrolyse by boiling for 30 min. on a water bath. Neutralise the cooled product with NaOH soln. (20%), and add conc. aq. NH_3 (2 ml) and HIO_4 soln. (2%) (1·5 ml). After 5 min. adjust the pH to 1 with HCl and extract the soln. with ether (3 × 25 ml). Reduce the vol. of the extract, transfer the residue to Whatman No. 3 paper and chromatograph by the descending technique with n-butanol - conc. aq. NH_3 (4:1) as solvent. The vanillin spot can be identified in u.v. light, then eluted with 0·1N-NaOH (16 ml) (2 hr.). After dilution of the eluate with 0·1N-NaOH, the extinction is measured at 347, 355 and 360 mμ against a blank.

J. ZÝKA

2561. **Direct ultra-micro glucose oxidase method for determination of glucose in biological fluids.** G. R. Kingsley and G. Getchell (Clin. Biochem. Lab., Vet. Admin. Center, Los Angeles, Calif., U.S.A.). *Clin. Chem.*, 1960, **6** (5), 466–475.—Mix plasma (0·02 ml) with peroxidase buffer reagent (4·5 ml), prepared by dissolving 5 mg of peroxidase in 59 ml of 0·1N-NaOH and 125 ml of 0·1M-KH_2PO_4, diluting to 500 ml with H_2O and adding 5 ml of 1% *o*-dianisidine in methanol. Add a 0·4% filtered aq. soln. of glucose oxidase (0·5 ml) and incubate for exactly 30 min. at 37° in a water bath. Add 50% (v/v) H_2SO_4 (1·5 ml) slowly with continuous mixing, place the tube in cold water for several minutes, then read the colour at 530 mμ. Prepare a blank with plasma (0·02 ml), adding the H_2SO_4 before incubation. Prepare standards containing 50 to 300 mg of glucose per 100 ml of 0·25% benzoic acid and treat as for the plasma. Urine is pre-treated by mixing 1 ml with H_2O (19 ml), adding Lloyd's reagent (1·5 g) and Norit charcoal (50 mg), shaking for 6 min. and filtering. The filtrate (0·02 ml) is used for the determination.

H. F. W. KIRKPATRICK

2562. **Determination of free myoinositol in biological fluids and tissues.** F. C. Battaglia, G. Meschia and D. H. Barron (Yale Univ. Med. Sch., New Haven, Conn., U.S.A.). *Biochim. Biophys. Acta*, 1960, **44** (2), 354–355.—The free myoinositol ($\lesssim$ 0·3 mg) in the sample is extracted if necessary by grinding with water, proteins are pptd. with $Ba(OH)_2$ - $ZnSO_4$ and, after centrifuging, the supernatant liquid is de-ionised and evaporated to dryness; the residue is dissolved in water to a concn. of 1 μg per μl. Descending chromatography of 50 to 400 μg is carried out on Whatman No. 1 paper with ethyl acetate - pyridine - water (2:1:2) for 16 hr. The appropriate area is then cut out and eluted with water, and the soln. is treated with 0·25M-$NaIO_4$. After heating this mixture at 100° for 20 min. the formic acid produced is determined by titration. W. H. C. SHAW

2563. **Determination of pentosans. V. Colorimetric determination of furfuraldehyde in the presence of 5-hydroxymethylfurfuraldehyde.** P. O.

Bethge and J. H. Eggers (Wood Chem. Dept., Swedish Forest Products, Stockholm). *Svensk Papp-Tidn.*, 1960, **63** (21), 745–748 (in English).—Two methods, considered to be best suited for the routine analysis of Tollens' distillates, have been examined and compared. Both, an orcinol method and an aniline method, have approx. the same reproducibility and are suitable for the determination of furfuraldehyde in the presence of 5-hydroxymethylfurfuraldehyde. The aniline method is more sensitive and should be preferred when samples of low pentosan content are analysed. The orcinol procedure is more convenient to use and is better for the routine analysis of normal samples.

P. PEDERSEN

2564. **Determination of ketone bodies in blood.** D. Glaubitt (I Med. Univ.-klin., Hamburg-Eppendorf). *Arzneimittel-Forsch.*, 1960, **10** (10), 837–845.—The specificity, sensitivity and precision of the alkaline iodine, alkaline salicylaldehyde, alkaline 2-furaldehyde, 2,4-dinitrophenylhydrazine, Na phenolphthalein-α-hydroxysulphonate, Denigès' reagent and Scott-Wilson alkaline $Hg(CN)_2$ methods are discussed, and interfering substances are listed. The determination of β-hydroxybutyric acid (**I**) by oxidation with chromic acid to acetone is also discussed. The use of factors to correct for acetone, derived from the total acetone fraction (acetone plus acetoacetic acid) (**II**) is not recommended; **I** and **II** should be determined separately, unless only approx. values for **I** are required. (129 references.)

A. G. COOPER

2565. **Detection of micro amounts of phenylpyruvic acid in urine.** Toshiro Murata, Akira Matsukawa and Yaeko Nakajima (Dept. of Hygienic and Forensic Chem., Univ. Kumamoto, Japan). *Kumamoto Pharm. Bull.*, 1959, (4), 256–263.—Urine (0·01 ml) is spotted on filter-paper and 0·005 ml of citrate buffer (pH 2·2) is dropped on to the spot. After drying, the spot is sprayed with 1% aq. $FeCl_3$. A green colour is produced by amounts of phenylpyruvic acid > 1·26 μg. Direct determination is made by adding 5 ml of 0·28% 2,4-dinitrophenylhydrazine in N-HCl to 5 ml of filtered urine and, after 30 min. at room temp., adding 4 ml of N-NaOH, mixing, adding 24 ml of H_2O, and measuring the extinction of the red soln. at 440 mμ.

H. F. W. KIRKPATRICK

2566. **Determination of bile pigments. I. Standard of purity for bilirubin.** R. J. Henry, S. L. Jacobs and N. Chiamori (Bio-Science Res. Found., Los Angeles, Calif., U.S.A.). *Clin. Chem.*, 1960, **6** (6), 529–536.—A method for the purification of commercial samples of bilirubin is described. The suggested standard for pure bilirubin is a molar extinction coeff. at 453 mμ in $CHCl_3$ of 60,100, the mol. wt. being taken as 584. The value at 545 mμ for pure azobilirubin is 64,100, based on an equiv. amount of bilirubin, when the diazo reaction is carried out as follows. Dissolve the bilirubin in 0·2% Na_2CO_3 soln. in the dark at room temp. and use within 1 hr. of preparation. To 1 ml of diazo reagent and 4 ml of H_2O add a mixture of 4·9 ml of methanol and 0·1 ml of the bilirubin soln. containing 20 μg of the product. Read at 545 mμ after 40 min. against a H_2O blank.

H. F. W. KIRKPATRICK

2567. **Direct spectrophotometry of total serum bilirubin in the newborn.** S. Meites and C. K. Hogg (Columbus Children's Hosp., Ohio, U.S.A.). *Clin. Chem.*, 1960, **6** (5), 421–428.—Serum is diluted 1 in 20 with Sörensen's phosphate buffer (pH 7·4) and the extinction is measured at 455 mμ and 575 mμ. The concn. of bilirubin is calculated from an equation derived from the determination of the absorption constant for the apparatus with standard haemoglobin and bilirubin soln. Errors due to haemolysis of the serum are thus avoided.

H. F. W. KIRKPATRICK

2568. **Vitamin B_{12} in human blood and serum. I. Comparison of microbiological assays using normal subjects.** H. Baker, O. Frank, I. Pasher and H. Sobotka (Mt. Sinai Hosp., New York, U.S.A.). *Clin. Chem.*, 1960, **6** (6), 578–581.—It is concluded from comparative assays that *Ochromonas malhamensis* provides the highest specificity.

H. F. W. KIRKPATRICK

2569. **Fluorimetric estimate of coumestrol on paper chromatograms.** A. L. Livingston, E. M. Bickoff, J. Guggolz and C. R. Thompson (Western Regional Res. Lab., Agric. Res. Service, U.S. Dept. of Agric., Albany, Calif.). *Anal. Chem.*, 1960, **32** (12), 1620–1622.—By using water-acetic acid (1:1) and Whatman No. 1 paper, and spotting with 2-μl portions of coumestrol in acetone, well-defined chromatograms can be obtained. The u.v.-excited fluorescence of the coumestrol spot varies linearly with the amount of coumestrol in the range 0·2 to 1 μg, provided that the aperture of the photocell is greater than the diameter of the spot. The coeff. of variation is ≃ 7%.

R. M. ROWLEY

2570. **Paper-electrophoretic determination of caeruloplasmin.** P. Bianchini and B. Osima (Lab. Ricerche Crinos, Ind. Farmacobiol., Milano, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1960, **36** (22), 1284–1288.—The determination and localisation of the serum cuproprotein caeruloplasmin are effected by paper-electrophoretic separation of serum proteins and examination of the enzyme oxidising action of the separated fractions on adrenaline, which develops a red colour. Blood serum (0·03 ml) is deposited in duplicate on strips of Whatman 3MM paper and subjected to electrophoresis in acetate-barbitone buffer (pH 8·6) at 4 V per cm for 15 hr., after which the strips are air-dried and cut into 1-cm sections, each of which is separately eluted for 2 hr. with water (2 ml). To each eluate is added a soln. of adrenaline (100 μg per ml) in acetate buffer (pH 5) (3 ml). After 5 hr. at 37° the extinction at 480 mμ is read. The intensity of the colour is a measure of the oxidase activity. Peaks of activity occur along the paper at positions corresponding to α_1- and α_2-globulins, indicating the existence of two enzymes and an association of activity and hence of caeruloplasmin with these proteins, but there is a difference in pattern in different species. Each serum shows two peaks; in rat and bovine sera the preponderant activity is associated with α_1-A globulin; in rabbit, human, guinea-pig and equine sera the main activity is associated with α_2-globulin. Bovine serum differs from others in that the second activity peak is associated with the β-globulin. There is fair concordance between the results for oxidase activity associated with α_2-globulin in this test with those obtained in Akerfeldt's test (*Science*, 1957, **125**, 117), but none between the α_2-A results and those obtained by Ravin (*Lancet*, 1956, **i**, 726). The total amount of blood caeruloplasmin is relatively the same in different species.

J. I. M. JONES

2571. **Rapid and precise method for the determination of urea.** J. K. Fawcett and J. E. Scott (Surgical Unit, St. Mary's Hospital, London, England). *J. Clin. Path.*, 1960, **13** (2), 156–159.—The reaction of ammonia with sodium phenoxide and hypochlorite, in the presence of sodium nitroprusside as a catalyst, to produce a blue colour is used to determine the amount of ammonium carbonate liberated by the hydrolysis of urea with urease. The sample diluted to contain between 1 and 5 μg of urea (1 ml) is incubated at 37° for 5 min. with phosphate buffer (0·006% of KH_2PO_4 and 0·002% of $Na_2HPO_4.2H_2O$) containing about 200 Sumner units of urease per 100 ml (1 ml). The following reagents are then added immediately and successively—2·5% phenol in 0·312N-NaOH (2 ml), 0·01% sodium nitroprusside soln. (3 ml) and ≃ 0·02N-NaOCl (3 ml). The extinction is read at 630 mμ after setting aside the soln. in the dark for 15 min. at 27° or 30 min. at 19°. The precision and accuracy of the method are examined and the results of recovery experiments are reported.

R. A. Brenan

2572. **Quantitative interpretation of polarographic waves for low concentrations of organic depolariser. Application of blank curves in tests on standard adenine solutions.** H. Panusz, M. Gross and B. Filipowicz (Dept. of Physiol. Chem., Acad. Med., Łódź, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 645–655.—The curves obtained in the polarography of standard adenine solutions are too deformed for interpretation by the parallel-line method, mainly owing to H^+ discharge at current values exceeding the diffusion current. The subtraction of corresponding blank-curve potentials converts the test graph into a curve of theoretical shape, in which the heights are proportional to the concentration of adenine within a range of 2·65 to 10·8 μg per ml. A graphical method of interpretation based on 45° tangents is described, and is claimed to be more accurate than other graphical methods.

P. Brych

2573. **Separation and estimation of purine and pyrimidine bases from a heated suspension of *Micrococcus flavius*.** K. W. Gerritsma and H. P. Levius (Univ. for Christian Higher Educ., Potchefstroom, S. Africa). *J. Pharm. Pharmacol.*, 1960, **12** (Suppl.), 176T–185T.—Guanine, cytosine, uracil, adenine and thymine are separated on Whatman No. 1 paper by ascending chromatographic development for 24 hr. at 20° with n-butanol - H_2O, and identified by the shapes of the u.v. absorption spectra. The bases can be determined by elution of the spots with H_2O (4 ml) and spectrophotometry at 260 mμ. Recoveries are mostly > 95%.

A. R. Rogers

2574. **Fluorimetric determination of creatine.** R. B. Conn, jun. (Dept. of Lab. Med., Univ. Minnesota, Minneapolis, U.S.A.). *Clin. Chem.*, 1960, **6** (6), 537–548.—To the serum or blood (1 ml) add H_2O (15 ml), 0·3N-$Ba(OH)_2$ (2 ml) and 5% $ZnSO_4$ soln. (2 ml), mix and filter through a fine filter-paper. To the filtrate (2 ml) add a 1% soln. of ninhydrin in 95% ethanol (1 ml) and a 10% soln. of KOH in 95% ethanol (1 ml), mix immediately and take fluorimetric readings 5 min. after addition of the KOH soln., with an excitation wavelength of 410 mμ and reading at 525 mμ. Freshly prepared standard soln. containing 0·05, 0·10 and 0·20 mg of creatine per 100 ml are run with each set of determinations and are read against a H_2O blank, whilst the test soln. are read against a filtrate blank prepared with H_2O in place of serum. To determine creatine in urine, shake 15 to 20 ml of a 1 in 50 dilution of the sample in a 50-ml flask with 3 g of Amberlite IRA-401 resin, prepared by immersion in 0·1N-NaOH followed by thorough washing. Allow the resin to settle and treat 2 ml of the supernatant fluid as described above for the filtrate. A quinine standard (2 mg per litre in 0·1N-H_2SO_4) is used for setting the sensitivity of the fluorimeter and checking calibration.

H. F. W. Kirkpatrick

2575. **Infra-red identification of the *N*-methyl group in substituted amino-acid hydrochlorides.** C. C. Watson (Dominion Lab., D.S.I.R., Wellington, New Zealand). *Spectrochim. Acta*, 1960, **16** (11–12), 1322–1327 (in English).—Assignments are given for bands in the 1400 to 1500-cm^{-1} region, which should aid in the identification of the *N*-methyl group of mono-, di- and tri-methylamino-acids. Any effect on intensity caused by reduction in the charge on the nitrogen atom is said to be greater than that caused by a change in the number of methyl groups. It is suggested that vibrations other than those of the N–CH_3 group are responsible for absorptions at 1438 cm^{-1}.

E. G. Cummins

2576. **Micro-analysis of amino-acids. III. Modified ninhydrin reagent for use in a quantitative determination by paper partition chromatography.** Takeo Tsukamoto and Tetsuya Komori (Pharm. Inst., Med. Fac., Univ. of Kyushu). *Chem. Pharm. Bull., Japan*, 1960, **8** (10), 913–917.—A reagent previously described (Tsukamoto *et al.*, *Ibid.*, 1957, **5**, 363) consisting of a mixture (1:1) of 2% ascorbic acid in HPO_3 soln. and 2% ninhydrin (**I**) in 2-methoxyethanol, has occasionally been found to give cloudy soln. and high blanks. The present reagent is stated to avoid this. *Procedure*—To prepare the reagent, dissolve **I** (250 mg) in peroxide-free 2-methoxyethanol (25 ml). Pass a stream of N through the soln. for 30 min. Add a soln. of ascorbic acid (50 mg) in 1% HPO_3 soln. (25 ml) and dilute to 50 ml with 1% HPO_3 soln. Keep the reagent in the dark at 5° for 1 day before use. Locate the spots on the chromatogram with 0·06% **I** soln. in ethanol. Cut out the spots and 2 or 3 blanks (≃ 2 sq. cm). Place each in a test-tube (15 cm × 1·5 cm), add 0·1M-NaOH (0·1 ml) and set aside overnight in a desiccator over H_2SO_4 at reduced pressure. Add 0·01M-citric acid (0·45 ml) and H_2O (0·5 ml) and shake. Add the reagent (1·0 ml) and citrate buffer (pH 5·3 ± 0·02) (0·5 ml), shake, and heat at 100° for 20 min. Cool, dilute to 10 ml with 50% ethanol and read the extinctions at 570 mμ (440 mμ for proline and hydroxyproline). The colouring relative to alanine ranged from 0·77 for ammonia to 1·34 for phenylalanine. A blank of 0·04 to 0·05 was consistently obtained. The mean recovery of amino-acids (0·4 mμmole) subjected to one-dimensional paper chromatography ranged from 80% for histidine to 115% for glycine. Mean errors were ± 2% to ± 5% (9 determinations).

G. Russell

2577. **Paper chromatography of complex biological materials by solvent re-development without prior removal of salts or proteins.** A. E. Pasieka (Lab. of Hygiene, Dept. of National Health and Welfare, Ottawa, Canada). *Canad. J. Biochem. Physiol.*, 1960, **38** (10), 1137–1147.—The separation of amino-acids, peptides and sugars from

complex biological mixtures containing high concn. of proteins and salts is effected, without previous removal of the salts or proteins (which normally interfere), by re-developing the chromatograms several times, with intermediate drying between developments. The extent of separation is limited only by the length of paper used. The process is described and illustrated for amino-acids and peptides in an acid hydrolysate of lactalbumin, amino-acids and sugars in hydrolysates of bacterial cells from staphylococcal vaccines, and a tissue-culture medium containing amino-acids in the presence of high salt and protein concn. The chromatograms were prepared by descending chromatography on 22·5-in. strips of S. & S. 597 or Whatman 3MM paper, and developed for 2 to 4 successive 18-hr. periods, with intermediate drying, with n-butanol - acetic acid - water or n-butanol - ethanol - water mixtures. Synthetic tissue-culture media (Morgan *et al.*, *J. Nat. Cancer Inst.*, 1955, **16**, 557), in which the ratio of NaCl to total amino-acids was 7:1 and that of NaCl to individual amino-acids ranged from 50 : 1 to 800 : 1, were used. The addition of 20% of human serum did not prevent clear separation. Sugars and amino-acids were identified by separate staining on twin chromatograms. Complete separation from salts and proteins was effected by two-dimensional chromatography with three solvent developments in each direction, with intermediate drying. Quantitative determination is then possible by photo-electric scanning of the stained spots, or spectrophotometrically after elution of individual spots. Successive 18-hr. developments with intermediate drying gives a clearer separation than does continuous development for the same total period. Reproducibility is very good if the conditions, especially the water concn., are controlled.

J. I. M. JONES

2578. **Oxidations with periodate. I. Determination of serine and threonine via the aldehydes and ammonia formed during oxidation by periodate.** L. Maros, I. Molnár-Perl and E. Schulek (Inst. f. Anorg. u. Anal. Chem., L. Eötvös Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1960, **24** (2), 213–222 (in German).—Three methods are described for the determination of serine and threonine (5 to 50 mg) after oxidation with periodate. (*i*)—The formaldehyde and acetaldehyde formed by serine and threonine, respectively, are determined by the bisulphite - cyanide method of Schulek and Maros (*Anal. Abstr.*, 1959, **6**, 1359). (*ii*)—The ammonia formed is determined by distillation in the presence of Na_2SO_3 to eliminate the effect of aldehydes. (*iii*)—The excess of periodate is back-titrated. The error is ± 0·5%.

E. C. BUTTERWORTH

2579. **Factors affecting the uptake of Lissamine green by serum proteins.** C. J. Brackenridge (Biochem. Dept., Royal Perth Hospital, Perth, W. Australia). *J. Clin. Path.*, 1960, **13** (2), 149–155.—It is shown that the grade of paper, separate and combined denaturation and staining times, temp. and concn. of staining soln., concn. of denaturant, and amount and type of protein all influence the uptake of Lissamine green (C.I. Acid Green 7) by filter-paper impregnated with serum proteins. Optimum conditions can be determined and a linear relationship obtained between dye uptake and protein concn. in electrophoretically separated protein fractions. R. A. BRENAN

2580. **Non-ionic surfactants in paper electrophoresis [of serum proteins].** W. D. Graham (Midwest Med. Res. Found., 3241 Victor Place, Wichita, Kans., U.S.A.). *Clin. Chem.*, 1960, **6** (5), 413–420.—The inclusion of 0·05% of certain alkylphenyl ethers of polyoxyethylene glycol (*e.g.*, Tergitol NP35) in the buffer soln. produces patterns that may be subdivided into 12 fractions—albumin, α_1-globulin, three α_2-globulins, three β-globulins, and four γ-globulins. Lipoproteins migrate at a reduced rate, but glycoproteins are not significantly affected by the addition.

H. F. W. KIRKPATRICK

2581. **Simple method for the determination of serum haptoglobins.** J. A. Owen, F. C. Better and J. Hoban (Clin. Biochem. Lab., St. Vincent's Hospital, Melbourne, Australia). *J. Clin. Path.*, 1960, **13** (2), 163–164.—A colorimetric procedure based on the peroxidase activity of haptoglobin - methaemoglobin complexes is described. The serum is mixed with methaemoglobin (prepared from human haemoglobin by oxidation with potassium ferricyanide), guiacol and H_2O_2, and the resulting colour is read in an absorptiometer. The concn. of haptoglobin is obtained from a calibration curve and is expressed in terms of bound methaemoglobin. R. A. BRENAN

2582. **Assay of fibrinogen in small blood samples.** H. D. Wycoff (Dept. of Biochem., Med. Coll. of Georgia, Augusta, U.S.A.). *Clin. Chem.*, 1960, **6** (5), 429–433.—A sample of whole blood (0·2 ml) is mixed in the syringe with isotonic citrate - phosphate buffer (McIlvaine) (pH 6·6) to a vol. of 0·6 ml. The fluid is centrifuged in a special tube to determine the packed-cell vol., and the dilution factor of the supernatant fluid is then calculated. The fibrinogen is determined in the plasma by coagulating with thrombin, collecting the clot on tared glass needles, rinsing with H_2O and ethanol, drying at 80° for 30 min. and weighing.

H. F. W. KIRKPATRICK

2583. **Differential colorimetric analysis of some deoxyribosyl compounds.** L. D. Saslaw and V. S. Waravdekar (Armed Forces Inst. Path., Washington, D.C., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **90** (2), 239–244.—In the method described, the nucleosides are hydrolysed at pH 2 and then oxidised with periodate at room temp. to give malonaldehyde, which is determined colorimetrically with thiobarbituric acid. Under these conditions nucleotides are not oxidised but do give the reaction when oxidised at 70°. The method is adapted for the separate determination of free deoxyribose, its 5-phosphate, and purine deoxyribo-nucleosides and -nucleotides in admixtures. W. H. C. SHAW

2584. **Oscillographic polarography of deoxyribonucleic and apurinic acids.** E. Palaček (Inst. of Biophysics, Acad. Sci., Brno, Czechoslovakia). *Biokhimiya*, 1960, **25** (5), 803–807.—Highly polymerised deoxyribonucleic acid (**I**) is extracted from glandular material with NaCl soln. and deproteinised with $CHCl_3$ - amyl alcohol or with an anionic detergent. Apurinic acid and **I** exhibit cut-ins with M-ammonium formate, KCl or NaCl soln., dil. KOH or NaOH soln. and soln. containing Ni^{2+} or Co^{2+} as basal electrolytes. The method may be used to follow the course of denaturation and to estimate its extent; it is simple, but less sensitive than spectrophotometric measurement.

Its main practical value lies in the determination of small amounts of protein in **I** with Co^{3+} or Ni^{3+} soln. as basal electrolytes; large amounts of protein do not interfere. K. R. Cook

2585. **Detection of purines, pyrimidines and their derivatives.** V. Habermann (Med. Fac., Charles' Univ., Prague, Czechoslovakia). *Biokhimiya*, 1960, **25** (5), 891–896.—The compounds are chlorinated on the paper before being located. *Procedure*—Pass the chromatogram or electropherogram through 96% ethanol - acetone (1:1). Remove the excess of solvent and immerse the chromatogram in fresh 10% HCl - 1% $KMnO_4$ soln. (1:1) for 10 min. To detect the chlorinated derivatives, immediately plunge the chromatogram into fresh 0·05M-KI - satd. *o*-tolidine soln. in 2% acetic acid (1:1), or 0·05M-KI - satd. benzidine soln. in acetic acid (1:2). After 2 to 3 min. wash the chromatogram with 2% acetic acid and photograph it immediately. Alternatively, remove all traces of free Cl *in vacuo* and spray the chromatogram with 0·05M-KI - 2% starch soln. (1:1). In each case the compounds are revealed as intense blue spots on a white background. The method can be used for the detection of purines, pyrimidines, dihydropyrimidines, nucleosides, deoxynucleosides, nucleotides, deoxynucleotides and nucleic acids in microgram amounts. K. R. Cook

2586. **Chromatographic separation of niacin [nicotinic acid] and its derivatives on a preparative scale using the ChroMax column.** C. Ovenfors (Royal Inst. of Technol., Div. of Food Chem., Stockholm, Sweden). *Sci. Tools*, 1960, **7** (1), 1–5 (in English).—A series of chromatographic separations of nicotinic acid derivatives with a ChroMax pressurised paper column containing 200 g of paper are described. The five components (≃ 10 mg of each) of the mixture investigated (nicotinic acid, nicotinamide, N^1-methylnicotinamide, diphosphopyridine nucleotide and triphosphopyridine nucleotide) were separated successfully by a method in which three different solvent systems were applied successively during the same test run. These were n-butanol - 1·5M-aq. NH_3 (25:4), n-propanol - 0·1M-phosphate buffer (pH 6·8) (4:1), and n-propanol - 0·1M-phosphate buffer (pH 6·8) (11:9). P. Pedersen

2587. **Simplified technique for estimation of serum lipoprotein cholesterol.** R. L. Searcy, L. M. Bergquist, R. C. Jung, R. Craig and J. Korotzer (Los Angeles County Osteopath. Hosp., Calif., U.S.A.). *Clin. Chem.*, 1960, **6** (6), 585–597.—The lipoproteins are located on marker strips by means of a molybdophosphoric acid reagent. The cholesterol in the corresponding areas on unstained strips is eluted directly into a $FeSO_4$ - acetic acid mixture for colorimetric analysis. H. F. W. Kirkpatrick

2588. **Chromatographic separation of oestrone, oestradiol and oestriol on Florisil columns.** A. Brancaccio, B. D'Alessandro and M. G. Aurilia (Ist. Semeiotica Med., Univ. Napoli, Italy). *Biochim. Appl.*, 1960, **7** (5), 277–280.—Dried residues containing oestrone (**I**), oestradiol (**II**) and oestriol (**III**) are dissolved in dichloromethane and passed through a chromatographic column (1 cm × 10 cm) of activated Florisil (60 mesh) prepared with the same solvent. Elution of **I** and **II** is effected with dichloromethane containing 4% of acetone (50 ml); **III** is eluted subsequently with dichloromethane containing 20% of ethanol (50 ml). From 16 μg of pure **I**, **II** and **III** on separate columns, 15, 15·5 and 15 μg, respectively, were recovered, and, from 30 μg of a mixture of 10 μg of each, 19 μg of **I** plus **II** and 9 μg of **III** were recovered. J. I. M. Jones

2589. **Spectrophotometric determination of oestriol. Experiments with David's arsenate reaction.** K. F. Støa (Hormonlab., Univ., Bergen, Norway). *Medd. Norsk Farm. Selsk.*, 1960, **22** (10), 189–197.—Experiments with David's arsenate reaction (*Acta Brev. Neerl. Physiol.*, 1934, **4**, 64) have shown that it is suitable as a quant. method, although only about half as sensitive as the Kober reaction. It is specific for oestriol, although other steroids give colours that do not interfere at 650 mμ. C. S. Howes

2590. **Determination of oestriol and of the oestrone - oestradiol fraction in urine.** M. F. Jayle, M. Heron and R. Scholler (École de Puériculture, 26 Boulevard Brune, Paris, France). *Bull. Soc. Chim. Biol.*, 1960, **42** (7–8), 923–943.—The urine (100 ml or one-tenth of the 24-hr. vol.) is hydrolysed by incubation with β-glucuronidase and extracted by allowing it to fall in a thin stream through a column of ether (800 mm × 24 mm), running it off from the bottom of the column and passing it through again so that 7 successive passages are made. The ether is washed by passage of 9% Na_2CO_3 soln. (2 × 75 ml). The oestriol is then extracted by running three 50-ml portions of 0·1N-NaOH containing 20% of NaCl through the column, each portion being given three successive runs. The NaOH soln. is neutralised and extracted with ether, the ether is evaporated and the extract is purified by the methylation method of Brown (*Anal. Abstr.*, 1955, **2**, 3161). The oestrone - oestradiol fraction is extracted by evaporating the original ether to dryness, dissolving the residue in benzene (50 ml) and extracting in the column with N-NaOH (3 × 50 ml), each portion being passed through the column three times. The NaOH soln. is boiled for 30 min. under reflux, cooled, and extracted with ether (100 ml) and the ether is rejected. The NaOH soln. is neutralised to phenol red with H_2SO_4, saturated with $NaHCO_3$ (about 10 g), and extracted with ether (200 ml). The ether is washed with 0·025M-H_2SO_4 (50 ml) and H_2O (50 ml) and is evaporated. The extracts are dissolved in abs. ethanol (5 ml) and aliquots (3 ml) are evaporated to dryness in tubes, 4% ethanolic quinol (0·2 ml) is added and evaporated under N to dryness. Then 13M-H_2SO_4 (0·6 ml) is added and the tubes are heated in boiling water for 20 min., shaking at 2 and 5 min. after commencing the heating. The tubes are cooled in ice, $NaNO_2$ soln. [0·01 g per litre in 31·5% (w/v) H_2SO_4] (1·4 ml) is added, and the tubes are again cooled in ice for 30 min. The rose colour is measured at 516, 476 and 556 mμ, and the Allen correction is applied to the reading at 516 mμ by subtracting the mean of the other two readings. Standards are prepared with oestrone and oestriol soln. H. F. W. Kirkpatrick

2591. **Chromatographic separation of pregnanediol from pregnanetriol on Florisil columns.** A. Brancaccio, B. D'Alessandro and M. G. Aurilia (Ist. di Semeiotica Med., Univ. Napoli, Italy). *Biochim. Appl.*, 1960, **7** (5), 281–285.—Dried

residues containing pregnanediol (**I**) and pregnanetriol (**II**) were dissolved in dichloromethane and passed through a chromatographic column (1 cm × 10 cm) of activated Florisil (60 mesh) prepared with the same solvent. **I** (50 μg) but no **II** was completely eluted with dichloromethane containing 7% of acetone (50 ml), and 50 μg of **II** was completely eluted with dichloromethane containing 20% of acetone (50 ml). With the former solvent (50 ml), from 10 μg of allopregnanediol and progesterone on separate columns, 9·5 and 10 μg, respectively, were also eluted, but no androsterone, dehydroisoandrosterone or 11-deoxycorticosterone (**III**); with the latter eluent, 5 μg of **III** was eluted from 10 μg on the column. J. I. M. JONES

2592. **Determination of urinary pregnanediol and pregnanetriol.** A. Brancaccio, B. D'Alessandro and R. Repole (Ist. di Semeiotica Med., Univ. Napoli, Italy). *Biochim. Appl.*, 1960, **7** (4), 183–186.—Hydrolyse the urine by heating it under reflux for 15 min. with 10% HCl in the presence of toluene (0·5 vol.). Cool, separate the toluene and re-extract the urine with toluene (0·33 vol.). Wash the combined extracts with 0·1N-NaOH (2 × 0·2 vol.), then boil with CaO till decolorised or pale yellow. Filter through a G3 filter that has been washed with boiling toluene and evaporate the filtrate to dryness *in vacuo*. Dissolve the residue in dichloromethane and chromatograph (*cf. Anal. Abstr.*, 1961, **8**, 2591). Measure the extinction of the eluates at 400, 435 and 470 mμ, and apply the Allen correction. A 90% recovery with good reproducibility is claimed.
J. I. M. JONES

2593. **Nomogram for the computation of the corrected colour value in 17-oxosteroid estimation by the Zimmerman reaction.** A. P. Kenny (Biochem. Dept., Clin. Lab., Victoria Infirmary, Glasgow, Scotland). *J. Clin. Path.*, 1960, **13** (3), 267.—The construction of a nomogram for use in the determination of 17-oxosteroids by the Zimmerman reaction, which incorporates the extinction correction recommended by the M.R.C. committee on clinical endocrinology, is described.
R. A. BRENAN

2594. **Quantitative evaluation of thin-layer chromatograms. II. Separation and determination of bile acids.** H. Gänshirt, F. W. Koss and K. Morianz (Firma Dr. Karl Thomae G.m.b.H., Biberach-an-der-Riss, Germany). *Arzneimittel-Forsch.*, 1960, **10** (11), 943–947.—Natural bile acids are partially separated on a plate of kieselguhr by development with toluene - acetic acid - water (10:10:1). The free bile acids are best separated with the upper layer of toluene - acetic acid - water (5:5:1), and the conjugated bile acids with butanol - acetic acid - water (10:1:1). For quant. determination, elute with 65% (w/w) H_2SO_4, heat at 65° for 1 hr. and measure the extinction at the absorption max. near 390 mμ. Quantities of ≃ 50 μg can be determined with a coeff. of variation of ± 3% (calculated from 10 replicates).
A. R. ROGERS

2595. **Infra-red spectra of bile acids and peptide-conjugated bile acids.** I. Fischmeister (Dept. of Med. Biochem., Inst. of Med. Chem., Univ. Uppsala, Sweden). *Ark. Kemi*, 1960, **16** (1–2), 151–169.—The solid-state spectra of the bile acids are noteworthy for their great specificity, which makes them well suited for the identification of unknown bile acids. This specificity is caused by differences of the carboxyl bands and of the methylene and methyl bands and the position of bands in the 9 to 10-μ region associated with C–OH stretching motions; 47 full spectra of bile acids and their sodium salts are given; 31 compounds have been investigated.
C. A. SLATER

2596. **Determination of proteinase activity with radioactive protein as the substrate.** I. I. Chikalo (Filatov Sci. Res. Inst. for Eye Diseases and Tissue Therapy, Ukraine). *Lab. Delo*, 1960, **6** (6), 52–54.—*Procedure*—Inject a rabbit sub-cutaneously with radioactive methionine (equiv. to 10,000 counts per g of live weight) labelled with ^{35}S and kill the animal after 6 hr. Grind the liver in phosphate buffer at pH 7·8, add normal saline soln., filter, add trichloroacetic acid (**I**) to the filtrate, filter off the protein residue, wash it free from active methionine with 5% **I** soln., dissolve it in 0·2% alkali soln., re-precipitate it and dry it in ethanol - ether, and suspend the dried protein (200 mg) in phosphate buffer (16 ml) at pH 7·8. Extract proteinase from commercial pancreatin (1 g) with normal saline soln. (6 ml) and mix the extract with glycerol and phosphate buffer (pH 7·8) in the ratio of 3:3:4. Incubate a mixture of protein suspension (16 ml), proteinase preparation (4 ml) and a drop of toluene at 37°. Just before incubation take two samples from the mixture. Precipitate protein in one sample with **I** (final acid concn. 5%), filter it off, place the filtrate (0·4 ml) on a plate, dry the plate and determine the radio-activity of the protein-free sample. Use the second sample for the determination of the total activity of the mixture. Correct for self-absorption and determine the percentage protein cleavage, taking the total activity of the sample (plus protein fraction) as 100%. The method is rapid, and produces results that agree closely with those by Kjeldahl determinations of residual N. K. R. COOK

2597. **Serum leucine aminopeptidase activity in normal pregnancy and in patients with hydatidiform mole.** R. Bressler and B. R. Forsyth (Dept. of Internal Medicine, Yale Univ. Sch. of Med., New Haven, Conn., U.S.A.). *New England J. Med.*, 1959, **261** (15), 746–748.—The serum leucine aminopeptidase activity is determined by the colorimetric assay of the 2-naphthylamine liberated by enzymatic hydrolysis of a synthetic substrate L-leucyl-2-naphthylamide hydrochloride.
R. A. BRENAN

2598. **Limitations in the diagnostic value of serum leucine aminopeptidase.** E. Hoffman, M. M. Nachlas, S. D. Gaby, S. J. Abrams and A. M. Seligman (Dept. of Surgery, Sinai Hospital, Baltimore, Md., U.S.A.). *New England J. Med.*, 1960, **263** (11), 541–544.—Serum (0·1 ml) is added to 0·08% L-leucyl-2-naphthylamide hydrochloride soln. (1 ml) and 0·1M-tri(hydroxymethyl)methylamine buffer (pH 7·4) (1 ml) and the mixture is incubated at 37° for 30 min. together with a control tube with the serum omitted. A soln. of Fast blue salt B (C.I. Azoic Diazo Component 48) (40 mg) in water (29 ml) and Tween 40 (1 ml) is prepared just before use; this soln. (3 ml) is then added to the reaction mixture and control tube. After 5 min., 4N-HCl (1 drop) is added to each tube and serum (0·1 ml) is added to the control tube. The extinction is read at 540 mμ, and the enzyme activity is determined by reference to a standard curve, prepared by substituting graded amounts

of 2-naphthylamine (0·07 to 0·28 μmole) for the substrate in the procedure. A unit of leucine aminopeptidase is defined as the enzymatic activity that will yield 0·001 μmole of 2-naphthylamine under the conditions of the assay. The normal range is 63 to 140 units. R. A. BRENAN

2599. **Use of a new assay in a study of serum alkaline phosphatase levels in two thousand hospital patients.** A. L. Babson, P. A. Read, G. E. Phillips and H. F. Luddecke (Warner-Lambert Res. Inst., Morris Plains, N.J., U.S.A.). *Clin. Chem.*, 1960, **6** (5), 495–500.—A commercially available tablet test, "Phosphatabs (alkaline)," run in parallel with the Bodansky method, yielded reliable semiquant. results. The use of this test for screening purposes when a high percentage of the assays yields normal results eliminates much tedious work.
H. F. W. KIRKPATRICK

See also Abstracts—**2444**, Cystine in plating baths. **2471**, Separation of sugars. **2643**, Lysolecithin in egg lecithin. **2678**, Desalting apparatus. **2679**, Ultrafiltration apparatus for body fluids.

Pharmaceutical analysis

2600. **Precision of some procedures in pharmaceutical analysis. II. Titrations.** A. R. Rogers (School of Pharmacy, Brighton Tech. College, Sussex, England). *J. Pharm. Pharmacol.*, 1960, **12** (Suppl.), 164T–170T.—Estimates have been made of the variation of the results obtained by students in 8 schools of pharmacy and by analysts in 5 industrial laboratories performing simple titrations. Coeff. of variation in the range 0·1 to 0·2% were typical of results of the industrial analysts. The corresponding figures for the students were mostly in the range 0·2 to 0·5%.
A. R. ROGERS

2601. **Identification and determination of nitrogenous organic bases with ammonium reineckate.** K.-T. Lee (Gov. Dept. of Chem., Outram Road, Singapore). *J. Pharm. Pharmacol.*, 1960, **12** (11), 666–676.—The reineckates of 5 opium alkaloids, 9 synthetic narcotics, 6 sulphonamides, 13 antihistamines and 8 other bases have been prepared and their decomposition temperatures and their solubilities at 5° and 27° are reported. To determine drugs as reineckates, dissolve the base or its salt (10 mg) in 0·1N-HCl (5 ml), add 2% aq. ammonium reineckate soln. (10 ml), cool to 0°, filter through sintered glass and wash the ppt. with ice-cold H_2O; dissolve the ppt. in acetone, dilute to 10 ml and measure the extinction at 525 mμ. Satisfactory assay of 39 drugs is reported.
A. R. ROGERS

2602. **New reagent for titrations in non-aqueous media. I. Determination of alkaloids by means of the hydrochloric acid complex of chloroaluminium isopropoxide.** I. Simonyi and G. Tokár (Verein. Arznei- und Nährmittelfabrik, Budapest). *Acta Chim. Acad. Sci. Hung.*, 1960, **25** (3), 305–311 (in German).—Results are discussed which show that the hydrochloric acid complex of chloroaluminium isopropoxide (**I**) behaves as a monobasic acid when undergoing salt formation with various alkaloids. A method is given for the determination of codeine, quinine, quinidine, papaverine, atropine, strychnine, chelidonine and amidopyrine, with 0·1N-**I** in $CHCl_3$. The deviation is ± 1% in the range 38 to 245 mg of alkaloid.

II. Determination of aniline, pyridine derivatives and esters of *p*-aminobenzoic acid by means of the hydrochloric acid complex of chloroaluminium isopropoxide. G. Tokár and I. Simonyi. *Ibid.*, 1960, **25** (3), 313–320 (in German).—A method is presented for the determination of aniline, *p*-anisidine, *p*-phenetidine, 2,6-diaminopyridine and esters of *p*-aminobenzoic acid. The recommended titrant is a solution of **I** in $CHCl_3$ and this can be used for the titration of any base having a dissociation constant $> 10^{-10}$. Ethyl orange or dimethyl yellow serve as indicators. The deviation is ≃ ± 1% in the range 20 to 150 mg.
R. PRESSER

2603. **Photometric and visual titration of certain alkaloids in glacial acetic acid using malachite green as indicator.** S. M. Tuthill, O. W. Kolling and K. H. Roberts (Mallinckrodt Chem. Works, St. Louis, Mo., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1678–1681.—Malachite green is a better indicator than crystal violet for the titration of weak bases in glacial acetic acid with $HClO_4$. Its extinction at 622 mμ decreases rapidly with increase in $HClO_4$ concn. Codeine, morphine, narcotine, papaverine and thebaine were titrated with 0·05M-$HClO_4$, with both potentiometric and photometric methods of end-point detection: the agreement between the two methods was excellent. Equally good results were obtained when the colour change was detected visually. Cryptopine can also be titrated, but the formation of a white suspension near the end-point prevents the use of the photometric method.
R. M. ROWLEY

2604. **Determination of total alkaloids in opium poppy plants.** Z. Wierzchowski, R. Aksanowski and M. Jurzysta (School of Agric., Lublin, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 671–681.—On the assumption that morphine, codeine, narceine, narcotine and papaverine are the main alkaloids, the possibility of pptn. with tungstosilicic acid was investigated. Limits of detectability ranged from 0·15 to 0·015 mg and limits of concn. from 1 in 7×10^3 to 1 in 2×10^4. The acid to alkaloid ratio in the ppt. is 1:4. The alkaloids are completely extracted by shaking twice with chloroform - ethanol (9:1). Precipitation is carried out from soln. in 0·05N-HCl and the alkaloids are calculated as the difference in weights of the ppt. after drying at 130° to 140° and ignition at 700°; 2·7% is allowed for loss of moisture. Detailed procedures are given.
P. BRYCH

2605. **Identification of papaverine by the coralyn reaction.** W. Awe, H. Halpaap and O. Hertel (Inst. f. Pharm. Technol., Tech. Hochschule, Braunschweig, Germany). *Arzneimittel-Forsch.*, 1960, **10** (11), 936–940.—Although microgram amounts of papaverine can be detected by the coralyn reaction (yellow - green fluorescence on heating with acetic anhydride and H_2SO_4) (*cf.* Awe, *Pharm. Zentralh.*, 1936, **77**, 157), related compounds in which the methylene bridge is substituted, or which lack two methoxyl groups in the benzene ring, fail to give the reaction.
A. R. ROGERS

2606. **Preparation and determination of solanine by ion exchange.** P. Patt and W. Winkler (Pharm.-Chem. Abteilung, Firma Dr. Madaus u. Co., Köln-Merheim). *Arch. Pharm., Berlin*, 1960, **293** (9), 846–853.—Material containing solanine (**I**) is

extracted with 3% ethanolic acetic acid, the extract is adjusted to ≃ 50% in ethanol and passed through a wide-meshed, cross-linked cation-exchange resin (Duolite C10). **I** is eluted with 10% ethanolic NH_3 and recovered by evaporation. The residue is dissolved in 3% ethanolic acetic acid, adsorbed on powdered cellulose, transferred to a column and eluted with the organic phase of butanol - acetic acid - water (4:1:5) on to a circular paper (S. & S. 2043b mgl) and developed for 8 hr. **I** and solanidine (**II**) are detected on one half of the chromatogram by blue colorations formed with 0·2% paraformaldehyde in 90% H_3PO_4. **II** being in the leading zone. The **I** zone of the other half of the chromatogram is cut out and extracted with 3% ethanolic acetic acid and the extract is evaporated to dryness. The residue is dissolved in 1% H_3PO_4 soln. and a 2-ml portion (≃ 300 μg of **I**) is mixed with the paraformaldehyde - H_3PO_4 reagent, heated at 50° for 1 hr., then cooled for 10 min. at 20°. The extinction is measured at 670 mμ against a blank not containing paraformaldehyde. A standard curve is prepared from soln. containing 20 to 260 μg of **I** per ml.

A. G. COOPER

2607. **A new colour test for the detection of some cardiac glycosides and aglycones.** H. P. Deys (Rijksuniv., Utrecht, Netherlands). *Pharm. Weekbl.*, 1960, **95** (21), 682–685 (in English).—*Procedure*—Evaporate a drop of the sample soln. to dryness in a porcelain dish, or place a few particles of the solid sample in it. Add a few crystals of oxalic acid and boric acid and 1 ml of ethanol, and evaporate on a boiling-water bath. The colour of the ethanolic mixture, the colour during evaporation and the colour of the residue are specific for the compound to be detected. The colours obtained for several cardiac glycosides are given. The limit of detection is ≃ 10 to 20 μg for digitoxin and 10 μg for gitoxigenin. The test can be applied to tablets or to pieces of filter-paper containing the sample without any previous extraction. M. J. MAURICE

2608. **Chemical assay of the cardiac glycosides of *Scilla maritima* L., var. *alba*.** B. Görlich (Knoll A.-G., Ludwigshafen a. Rh., Germany). *Arzneimittel-Forsch.*, 1960, **10** (9), 770–774.—*Procedure*—Extract the dried powdered material with ethanol, evaporate under reduced pressure and dissolve the residue in H_2O. Obtain two fractions by successive extraction with ethyl acetate - $CHCl_3$ - ethanol (4:5:1) and ethanol - $CHCl_3$ - H_2O (1:1:1). Evaporate the extracts under reduced pressure, dissolve the residues in methanol and determine the glycosides colorimetrically by the Liebermann reaction with acetic anhydride and H_2SO_4. Proscillaridin A, scillaren A, scilliglaucoside, scillicyanoside and other glycosides can be determined by chromatographic separation on a column of silica gel or a thin layer of Kieselgel G (Merck), with a 5% soln. of methanol in water-saturated ethyl acetate as solvent, or on paper with water-saturated ethyl acetate as solvent, followed by elution with methanol and colorimetry. A. R. ROGERS

2609. **Assay of digitalis.** J. G. Bhatt and A. D. Macdonald (Dept. of Pharmacol., Univ., Manchester, England). *J. Pharm. Pharmacol.*, 1960, **12** (12), 733–738.—The use of the outer wall of the guinea-pig right ventricle and of the rabbit auricle for the assay of digitalis has been reinvestigated, and the results obtained are compared with those by the methods of the B.P. 1958 and the U.S.P. XV. The isolated-auricle method is reasonably accurate, cheap and less time-consuming than other methods; it has the advantage that standard and unknown are compared on the same tissue. A. R. ROGERS

2610. **Analysis of some sympathomimetics. VII. Studies on the separation of sympathomimetics by Craig distribution.** K. König and R. Pohloudek-Fabini (Pharm. Inst., Ernst-Moritz-Arndt Univ. Greifswald, Germany). *Pharm. Zentralh.*, 1960, **99** (11), 683–691.—The distribution of ephedrine hydrochloride (**I**), pholedrine sulphate (**II**) and adrenaline hydrochloride (**III**) between various pairs of solvents has been compared by means of a Craig counter-current apparatus. **I** and **II** can be separated from **III** almost quant. in 24 stages by use of the two phases obtained by mixing phenol (240 g) with 0·02N-HCl (350 ml).

A. R. ROGERS

2611. **The determination of kanamycin in the presence of penicillin or streptomycin.** L. von Lorch, G. De Felip, S. Alberti and R. Negri (Lab. Microbiol., Ist. Sup. Sanit., Roma). *R. C. Ist. Sup. Sanit.*, 1960, **23** (9), 744–749.—Kanamycin in antibiotic mixtures containing penicillin (**I**) or streptomycin (**II**) is determined either by inactivating **I** or **II** or by using test organisms resistant to these antibiotics but not to kanamycin, or vice versa. Penicillin G (sodium salt) is inactivated by adding penicillinase soln. (3 ml) to 1 ml of antibiotic mixture (200 μg per ml) diluted to 10 ml and incubated for 24 hr. at 37°. **II** is inactivated by adding 2% cysteine hydrochloride soln. (1 ml) to the antibiotic mixture (9 ml), diluting to 1 in 200 and keeping warm for 2 hr. Kanamycin is not affected by either of these procedures. The organism used was *Micrococcus pyogenes* var. *aureus*. A mutant of this organism resistant to **I** was also used to determine kanamycin in admixture with **I**, and another mutant resistant to kanamycin was used to determine **I** in such a mixture or to determine **II** in an analogous mixture. Similarly, a mutant of *Bacillus subtilis* resistant to **II** was used to determine kanamycin in admixture with **II**. J. I. M. JONES

2612. **An agar diffusion microbiological assay for thiostrepton.** J. D. Levin, H. Stander and J. F. Pagano (Squibb Inst. Med. Res., New Brunswick, N.J., U.S.A.). *Antibiot. & Chemother.*, 1960, **10** (7), 422–429.—A large-plate paper-disc agar diffusion assay is described with *Micrococcus pyogenes* var. *aureus* (ATCC 6538P) as test organism. Standards are prepared in 80% aq. dimethyl sulphoxide containing 5, 2·5 and 1·25 units of thiostrepton per ml. Improved sensitivity and dose - response slope are attained by the inclusion of 1 to 3% of NaCl in the medium at pH 9. Modifications of the method are described for the assay of a formulated preparation and for the control of the concentration in milk following intramammary application to cows.

W. H. C. SHAW

2613. **Determination of panthenol in pharmaceutical preparations by microbiological assay with *Escherichia coli* 99-4.** C. G. Rogers and J. A. Campbell (Food and Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Canada). *Anal. Chem.*, 1960, **32** (12), 1662–1664.—The method depends on the turbidimetric measurement of the growth response of *E. coli* 99-4 to pantoic acid, which is produced by alkaline hydrolysis of

panthenol. It compares favourably in accuracy and precision with the inhibition method in which *Leuconostoc mesenteroides* P-60 is used (*cf.* Bird and McReady, *Anal. Abstr.*, 1959, **6**, 2753). Both methods are preferred to the *Acetobacter suboxydans* method (*cf.* Rubin *et al.*, *Anal. Chem.*, 1949, **21**, 823; 1951, **23**, 1689) in ease of handling and stability of response. The *E. coli* method is sensitive to 0·5 μg of pantoic acid per ml. Pantothenic acid interferes and must be removed immediately before assay. A. R. ROGERS

2614. **Ion-exchange method for the determination of cantharidin in cantharides.** W. Kamp (Pharm. Lab., Rijksuniv., Utrecht, Netherlands). *Pharm. Weekbl.*, 1960, **95** (24), 793–797.—*Procedure*—Mix 6·5 g of powdered drug with 15 g of washed sand and percolate with a mixture of $CHCl_3$ and HCl (100:1) until 200 ml of percolate is obtained. Distil off the solvent and boil the residue under reflux with 10 ml of 0·1N-NaOH for 15 min. Cool, add 50 ml of H_2O and pass the soln. through a column packed with Dowex 1-X2 (OH^- form). Wash the column with H_2O until the percolate is alkali-free, then elute the cantharidin with 150 ml of 2N-NaOH. Acidify the eluate and extract with $CHCl_3$. Evaporate the $CHCl_3$ soln. to dryness. The product obtained in this way has a m.p. of 208°. M. J. MAURICE

2615. **A new colorimetric method for the determination of chloral hydrate.** A. W. Archer and E. A. Haugas (Smith and Nephew Res. Ltd., Hunsdon Lab., Ware, Herts., England). *J. Pharm. Pharmacol.*, 1960, **12** (12), 754–760.—The method, which is based on the production of a stable blue cyanine dye, is suitable for the determination of chloral hydrate (**I**) in the presence of its decomposition products trichloroacetic acid, formic acid and $CHCl_3$. The hemi-acetal of **I** and the addition compound dichloral phenazone produce a blue colour in proportion to their **I** content; chloral formamide produces a green colour; butyl chloral hydrate produces a reddish-violet colour. **I** can be determined in pharmaceutical preparations with an accuracy comparable with that of the appropriate B.P. or B.P.C. method. *Procedure*—Mix an aq. soln. or extract of the sample (1 ml containing 50 μg of **I**) with 1·5% aq. quinaldine ethiodide soln. (1 ml) and isopropyl alcohol (6 ml), add 0·1N-ethanolamine (0·5 ml), dilute with H_2O to 10 ml, heat at 60° for 1 hr., cool and compare the extinction of the soln. at 605 mμ against a reagent blank with that of a similarly treated standard soln. of **I**. A. R. ROGERS

2616. **Determination of allyl isothiocyanate.** W. Fürst and W. Poethke (Inst. f. Pharm. u. LebensmittChemie, Friedrich-Schiller Univ., Jena, Germany). *Pharm. Zentralh.*, 1960, **99** (11), 674–677.—The argentimetric method of the D.A.B. VI gives spuriously high results for the assay of pure allyl isothiocyanate (**I**) and low results for the determination of **I** in mustard seed. The modified methods presented give correct results. *Procedure*—Heat gently a mixture of a 2 % soln. of **I** in ethanol (5 ml) with 25 % aq. NH_3 (5 ml) and ethanol (5 ml) for 10 min., then more strongly for another 10 min. Add 10 % NH_4NO_3 soln. (10 ml), cool, add 0·1N-$AgNO_3$ (50 ml), mix, dilute to 100 ml with H_2O and filter. To a 50-ml aliquot of the filtrate add 25 % HNO_3 (10 ml) and titrate with 0·1N-NH_4SCN, with $(NH_4)_2SO_4.Fe_2(SO_4)_3$ as indicator. To determine **I** in mustard seed, macerate the sample (5 g) with H_2O (100 ml) for 2 hr., add ethanol (50 ml), distil and collect 50 ml of distillate. Heat the distillate with 25% aq. NH_3 (10 ml), add 10 % NH_4NO_3 soln. (10 ml) and 0·1N-$AgNO_3$ (20 ml) and complete the determination as described above. A. R. ROGERS

2617. **The identification of derivatives of barbituric acid by X-ray analysis. X. Pentobarbitone, amylobarbitone and mixtures of the two compounds.** B. Jerslev and E. J. Ravn-Jonsen (Royal Danish School of Pharm., Copenhagen). *Dansk Tidsskr. Farm.*, 1960, **34** (8), 153–164; (9), 186 (a correction).—The polymorphism shown by pure pentobarbitone (**I**) and by amylobarbitone (**II**) and the behaviour of the binary system formed by the two compounds have been investigated. In mixtures of **I** and **II** the two compounds may be identified and the percentage composition may be determined by a combination of m.p. determination and X-ray powder analysis. In analysing mixtures containing up to 35% of **II**, the m.p. determination is of no value; in analysing mixtures containing up to 35% of **I**, X-ray analysis is useless; in the range 35 to 65% of **I** both methods are applicable. P. PEDERSEN

2618. **Qualitative and quantitative colorimetric analysis of orotic acid.** G. Banchi and E. Lomuto (Banchi & Moggi, Ind. Biochem., Firenze, Italy). *Farmaco, Ed. Prat.*, 1960, **15** (10), 606–616.—In the absence of specific colour reactions for orotic acid (**I**), non-specific reactions for purines and pyrimidine derivatives are used on oxidised **I**. Qual. reactions with a dimethylglyoxime - thiosemicarbazide reagent or resorcinol are described and methods for quant. determination with Folin - Ciocalteu reagent and with $FeCl_3$ are given. J. I. M. JONES

2619. **Determination of phenacetin in tablets.** C. M. P. Wirth (Sydney Ross & Co., Mexico). *Pharm. Acta Helv.*, 1960, **35** (11), 575–577 (in French).—The method is based on the procedure of Devi and Khorana (*Indian J. Pharm.*, 1953, **15**, 168, 193). A single determination takes ≃ 1 hr. The results of 12 replicate determinations of phenacetin in a sample of tablets of aspirin, phenacetin and caffeine ranged from 21·40 to 23·54%; the results by the method described previously (*Anal. Abstr.*, 1960, **7**, 1898) ranged from 21·64 to 23·12%. *Procedure*—Shake the powdered sample (containing 0·1 g of phenacetin) with 95% ethanol (50 ml) and filter through paper, rejecting the first 15 ml. Heat 0·5 ml of the filtrate with conc. HCl (5 ml), evaporate to ≃ 1 ml, dilute with H_2O (5 ml), cool in an ice bath and add 0·5% $NaNO_2$ soln. (1 ml). After 10 min. add 2% H_2SO_4 soln. (1 ml), 0·01% ethanolic thymol soln. (6·5 ml) and N-NaOH (6·5 ml) with shaking; dilute with H_2O to 50 ml, mix and measure the extinction at 500 mμ. A. R. ROGERS

2620. **Spectrophotometric determination of Mesocaine [mesidicaine].** J. Vachek (Res. Inst. Pharm. and Biochem., Prague). *Českosl. Farm.*, 1960, **9** (10), 505–506.—*Procedure for the substance*—Dissolve Mesocaine (diethylaminoacetmesidide) hydrochloride (5 mg) in 0·1N-HCl (100 ml) and measure the extinction at 222 mμ. Dihydroergotoxine methanesulphonate does not interfere. *For injections containing phenylbutazone*—To the sample (= ≃ 4 mg of Mesocaine) add N-HCl (1 ml) to precipitate phenylbutazone. After 5 min. add N-HCl (4 ml), shake and set aside for 10 min. Filter

off the precipitate on a 2-cm layer of Hyflo-Supercel washed with N-HCl (20 ml). Wash the vessel and the column with N-HCl (2 ml), dilute the combined eluates to 100 ml and measure the extinction at 222 mμ. J. ZÝKA

2621. **Some factors involved in multiple-spot formation in the paper chromatography of sympathomimetic amines in the presence of acids.** A. H. Beckett, M. A. Beaven and A. E. Robinson (School of Pharmacy, Chelsea Coll. of Sci. and Technol., Manresa Road, London, England). *J. Pharm. Pharmacol.*, 1960, **12** (Suppl.), 203T-216T.—The paper-chromatographic behaviour of a variety of amines, both alone and in the presence of acids in acidic, neutral and basic developing solvents, is reported. With a n-butanol - acetic acid - water solvent, multiple-spot formation by several pure amines was observed in the presence of the stronger organic acids. Many weaker acids affected the amines in a neutral solvent. The results emphasise the need for correct controls and the cautious interpretation of chromatograms of biological extracts, since the number of spots produced is not necessarily indicative of the number of bases present. A. R. ROGERS

2622. **Polarographic determination of mercaptothiamine.** M. Konupčík, M. Liška and F. Kupčík (Dept. Tech. Control, Farmakon, Olomouc, Czechoslovakia). *Českosl. Farm.*, 1960, **9** (10), 502–504.—*Procedure*—Dissolve the sample (250 mg) in N-H_2SO_4 (10 ml) and dilute with H_2O to 100 ml. To a 5-ml aliquot add N-H_2SO_4 (5 ml) and dilute with H_2O to 50 ml. Register the anodic wave of mercaptothiamine in a 10-ml aliquot after removing O with N ($E_{\frac{1}{2}} = -0{\cdot}26$ V). The results have an accuracy within ± 2% and are in good agreement with those of the bromatometric method (Buděšinský and Vaníčková, *Anal. Abstr.*, 1958, **5**, 2410). J. ZÝKA

2623. **Quantitative determination of pentetrazol [leptazol].** E. Andersson, M. Fors and J.-E. Lindgren (Swedish Pharmacopoeia Commission, Stockholm). *Acta Chem. Scand.*, 1960, **14** (9), 1957–1960 (in English).—The determination of leptazol by means of its complex with $CdCl_2$ was investigated, as the methods with CuCl were insufficiently accurate. The cadmium complex is almost insoluble in isopropyl alcohol - water, and, after isolation of the complex, the Cd is determined complexometrically. *Procedure*—To 0·15 g of sample dissolved in 2 ml of isopropyl alcohol - water (3:2) add 10 ml of fresh $CdCl_2$ soln. (15 g of $CdCl_2.2{\cdot}5H_2O$ dissolved in 40 ml of warm H_2O, filtered, cooled, and diluted to 100 ml with isopropyl alcohol). Swirl for 10 min. and filter through a 3G4 sintered glass filter. Transfer the ppt. completely to the filter with the filtrate, and wash it with isopropyl alcohol - water (9:1) (2 × 5 ml), then with isopropyl alcohol (3 × 10 ml). Dissolve the ppt. in 100 ml of hot H_2O, cool, add 10 ml of buffer soln. [6·75% (w/v) of NH_4Cl and 57% (v/v) of conc. aq. NH_3] and 5 drops of indicator soln. (0·5% of Eriochrome black T and 4·5% of hydroxyammonium chloride in methanol) and titrate at once with 0·1N-EDTA (disodium salt) (1 ml ≡ 6·909 mg of leptazol). C. S. HOWES

2624. **Determinations of acetazolamide and chlorothiazide.** J. Kráčmar and J. Vacek (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1960, **9** (10), 497–502—(*a*) *Titration in non-aqueous medium*—Dissolve the sample (30 to 100 mg of acetazolamide or chlorothiazide) in anhyd. pyridine (30 ml), add azo violet (**I**) or Alizarin yellow R (C.I. Mordant Yellow 1) (**II**) soln. (3 drops) as indicator and titrate with 0·1N-Na methoxide to a colour change from blue - violet to blue (with **I**) or from violet - red to violet (with **II**), or titrate potentiometrically. (*b*) *Spectrophotometry*: *for acetazolamide*—Dissolve the sample (0·1 g) by shaking for 10 min. in boiling H_2O (200 ml), cool and dilute to 500 ml. Dilute 5 ml of this soln. to 1 litre with methanol, or 0·01N-HCl or 0·01N-KOH, and measure the extinction at 265 mμ (for methanol soln.), 292 mμ (KOH) or 295 mμ (HCl). When analysing tablets, the undissolved matter must be filtered off. *For chlorothiazide*—Dissolve the sample (0·1 g) by gently heating in ethanol (50%) (70 ml) on a water bath, cool and dilute with the same solvent to 100 ml. Dilute a 2-ml aliquot with ethanol (50%) to 200 ml and measure the extinction at 280 mμ. The method can be used for the analysis of tablets after separating the undissolved matter by filtration. By a similar method, 5-acetamido-1,3,4-thiadiazole-2-thiol can be determined at 310 mμ and 5-amino-1,3,4-thiadiazole-2-thiol at 293·5 mμ in 0·01N-KOH medium. (*c*) *Paper chromatography*—For the separation use Whatman No. 1 paper with (*i*) n-butanol satd. with H_2O and the descending technique, (*ii*) n-butanol - anhyd. acetic acid - H_2O (5:1:4) (ascending technique), or (*iii*) n-butanol - conc. aq. NH_3 - H_2O (4:1:5) (ascending technique). For the detection, use Pb acetate soln. (15%) and observe the separated spots under a mercury-vapour lamp. Accuracies of ± 1% (titration) and ± 2% (spectrophotometry) were attained. J. ZÝKA

2625. **Ultra-violet spectrophotometric determination of chlorothiazide.** H. Marciszewski (Dept. Anal. Chem., Inst. Pharm., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (4), 617–624.—The u.v. absorption spectra of chlorothiazide (**I**) and the chief impurity 4-aminobenzene-6-chloro-1,3-disulphonamide (**II**) vary with the pH of the soln. At pH 10, **I** shows a minimum at 260 mμ and a maximum at 290 mμ, whilst the minimum and maximum positions for **II** are reversed. The extinctions of a soln. containing 4 to 12 mg per litre are measured at these wavelengths and percentages of **I** and **II** calculated from a formula provided, but < 2% of **II** cannot be satisfactorily determined. P. BRYCH

2626. **Physico-chemical studies of (1-methyl-2-pyrrolidyl)methyl benzilate methyl methosulphate [poldine methosulphate]. I. Determination of poldine methosulphate in the presence of its breakdown products.** D. O. Singleton and G. M. Wells (Beecham Res. Lab. Ltd., Brentford, Middx., England). *J. Pharm. Pharmacol.*, 1960, **12** (Suppl.), 171T-175T.—The method depends on the formation of a $CHCl_3$-soluble blue complex of poldine with ammonium cobaltothiocyanate, and it has been used for the determination of poldine methosulphate in stored tablets and linctuses. Benzilic acid, *N*-methylprolinol methyl methosulphate, unquaternised poldine, caffeine, quinine, codeine, ephedrine and atropine do not interfere. *Procedure*—Shake an aq. soln. of the sample (5 ml containing 0·3 to 1·5 mg of poldine methosulphate) vigorously for 1 min. with 20 ml of an aq. soln. containing 3·75% of $Co(NO_3)_2.6H_2O$ and 15% of NH_4SCN, and set aside for 5 min. Extract the aq. layer by vigorous shaking with $CHCl_3$ (4 ×

5 ml). Centrifuge the combined extracts for 5 min. at 2000 r.p.m., and measure the extinction of the clear soln. at 322 mμ. Calculate by reference to a calibration curve prepared on the same day.
A. R. ROGERS

2627. **Colorimetric estimation of sulphanilamide and its derivatives in pharmaceutical products.** Ajit K. Sengupta, Sakti P. Sen and Ramesh Chatterji (Albert Davis Ltd., Calcutta, India). *Drug Standards*, 1960, **28** (6), 139–142.—The method of Bratton and Marshall (*J. Biol. Chem.*, 1939, **128**, 537) is recommended because of its precision, accuracy and suitability for routine assay of a number of samples at a time. The procedure is illustrated by the assay of sulphaguanidine and phthalylsulphacetamide in admixture in tablets.
A. R. ROGERS

2628. **Rapid determination of mercury compounds in crude phenylmercury acetate.** M. Wroński (Dept. Chem. Technol., Univ., Łódź, Poland). *Chem. Anal., Warsaw*, 1960, **5** (4), 601–604.—Total mercury is liberated by heating 50 to 200 mg of sample to fuming with conc. H_2SO_4, diluting and boiling with bromine water. After making the soln. alkaline with NaOH and aq. NH_3, Hg^{2+} are titrated with 0·05N-Na thioglycollate, with thiofluorescein as indicator. Mercuric acetate is determined in an aq. extract by titration before and after decomposition with bromine water. The residue insoluble in hot 80% acetic acid is filtered off and weighed as triacetoxymercuribenzene; after dilution of the filtrate with water, the pptd. diacetoxymercuribenzene is separated and the total mercury remaining in the clear soln. is again determined.
P. BRYCH

2629. **The assay of stilboestrol by the isotope dilution technique.** R. Fleming (School of Pharmacy, Univ. of London, Brunswick Square, London, England). *J. Pharm. Pharmacol.*, 1960, **12** (Suppl.), 217T–219T.—Mix the sample (1·5 g) with an ethanolic soln. of ^{14}C-labelled stilboestrol (30 μl containing ≃ 0·06 μC) and acetylate according to the method of the B.P. 1958. Filter through sintered glass (porosity 3) and dry the ppt. at 110° for 1 hr. Add 100 mg of the acetylated stilboestrol ppt. to 12 ml of phosphor soln. [mix naphthalene (80 g) with diphenyloxazole (5 g), 1,4-di-(5-phenyl-2-oxazolyl)benzene (5 mg), xylene (390 ml), dioxan (390 ml) and ethanol (235 ml)] and count for 100 sec.; correct for lost counts and background. Recoveries in 4 replicate determinations ranged from 97·5 to 101·5%.
A. R. ROGERS

2630. **Enzymatic method for the determination of prednisolone phosphate in pharmaceutical preparations.** P. F. G. Boon (Anal. Dept., Glaxo Laboratories Ltd., Greenford, Middx., England). *J. Pharm. Pharmacol.*, 1960, **12** (Suppl.), 159T–163T.—Prednisolone phosphate (**I**) is hydrolysed enzymatically to prednisolone (**II**), which is determined by u.v. spectrophotometry. A preliminary extraction with $CHCl_3$ removes **II** and other decomposition products which would otherwise interfere. This method cannot be used for the determination of **I** in preparations which contain also thioglycerol or nicotinamide. With slight modification, the method can be used for the determination of the 21-monophosphoric esters of hydrocortisone and dexamethasone. *Procedure*—Extract an aq. soln. of the sample (15 ml containing 2·5 mg of **I**) with $CHCl_3$ (2 × 25 ml) and wash the extracts with H_2O (2 ml). Dilute the combined aq. phase and washings with H_2O to 25 ml and mix a 5-ml aliquot with glycine buffer (pH 8·6) (5 ml), a soln. of 5% of $CaCl_2$ and 5% of $MgCl_2$ in glycine buffer (1 ml) and an aq. soln. of alkaline phosphatase (1 ml containing 1000 units) which has been purified by washing with $CHCl_3$. Incubate the soln. at 37° for 4 hr., cool, and extract with $CHCl_3$ (3 × 25 ml). Wash the combined $CHCl_3$ extracts with H_2O (2 ml) and reject the washings. Evaporate to dryness, dissolve the residue in ethanol (25 ml) and measure the extinction at the wavelength of max. absorption near 242 mμ.
A. R. ROGERS

2631. **Determination of aluminium in pharmaceutical preparations.** A. Kovách and G. Vastagh (Chem. Abteilung des Staatl. Inst. f. Hyg., Budapest). *Pharm. Zentralh.*, 1960, **90** (10), 595–601.—The method has been successfully applied to the determination of Al in tablets, ointments and other pharmaceutical preparations. *Procedure*—Mix the soln. (15 ml containing 5 to 10 mg of Al, preferably as sulphate) with acetate buffer (pH 4·6) (10 ml), add 0·05M-EDTA (disodium salt) (10 ml), heat to boiling for 3 or 4 min. and back-titrate while still hot with 0·05M-$CuSO_4$, with 4-(2-pyridylazo)resorcinol as indicator.
A. R. ROGERS

2632. **Rapid method for the determination of aluminium and magnesium in synthetic acid-soluble pharmaceutically used magnesium aluminium silicate.** H. Gänshirt, H. Scheffler and W. Altenschmidt (Firma Dr. Karl Thomae G.m.b.H., Biberach-an-der-Riss, Germany). *Arzneimittel-Forsch.*, 1960, **10** (11), 940–943.—Dissolve the sample (15 mg) in N-HCl (0·5 ml), dilute to 10 ml with H_2O and titrate with N-NaOH. Use recording potentiometric titration apparatus to plot the graph of pH as a function of vol. of N-NaOH. The curve shows end-points at pH values of about 2·5 (*a* ml) and 6 (*b* ml). Perform a blank titration (*c* ml). Calculate the amount of Al from $b - a$, and the amount of Mg from $c - b$. The coeff. of variation, estimated from 9 replicate determinations, is ± 0·63% for Al and ± 1·03% for Mg. The results agree well with those obtained complexometrically and gravimetrically.
A. R. ROGERS

See also Abstracts—**2658**, Determination of riboflavine. **2659**, Determination of ascorbic acid.

Food

Food and food additives, beverages, edible oils and fats, vitamins.

2633. **Application of the Karl Fischer method to the determination of water in sugar confectionery materials.** D. Sandell (Process and Product Res. Sect., Geo. Bassett & Co. Ltd., Sheffield, England). *J. Sci. Food Agric.*, 1960, **11** (11), 671–678.—The construction and use of an apparatus for the convenient extraction and titration of water in confectionery materials with Karl Fischer reagent (**I**) by the dead-stop end-point technique are described in detail. Samples are heated with dry methanol for a time depending on the nature of the material, stirred with an excess of **I** and then back-titrated with a standard soln. of water in

methanol. Details of sample preparation and necessary heating times are tabulated for a large number of confectionery raw materials, semi-finished and finished products. The method is rapid (from 7 to 40 min.) and sensitive. Results are reproducible (± 1% of the water content) and agree with those of oven-drying methods in many cases, but there are discrepancies in others, and possible reasons for these are discussed.

E. C. APLING

2634. **Damaged starch. Quantitative determination in flour.** R. M. Sandstedt and P. J. Mattern (Dept. of Biochem. and Nutrition, Univ. Nebraska, Lincoln, U.S.A.). *Cereal Chem.*, 1960, **37** (4), 379–390.—Duplicate samples (1 g) of flour are placed in Erlenmeyer flasks with some ignited quartz sand, and to each sample are added 40 ml of buffer soln. (pH 4·6 to 4·8) and 6 ml of malt enzyme soln., all the soln. being brought to 30° before mixing. The temperature is maintained at 30° while stirring the mixture for exactly 1 hr. for the first sample and 2 hr. for the second. Then 3·58N-H_2SO_4 (2 ml) is added to each flask and mixed, followed immediately by 12% sodium tungstate soln. (2 ml). After 2 min. each mixture is filtered, the first 10 drops of filtrate being discarded. An aliquot (5 ml) of the filtrate is then mixed with 0·1N-alkaline ferricyanide reagent (prep. described) (10 ml) and the test-tube is immersed in a boiling-water bath for 20 min. After cooling, the soln. is transferred to a flask, soluble starch - KI soln. (1 ml) is added and the mixture is titrated with 0·1N-$Na_2S_2O_3$ to the discharge of the blue colour. The amount of ferricyanide consumed is calculated from the titration value and converted to maltose by means of a conversion table. The amount of maltose (%) is plotted against time, and the straight line extrapolated to zero time to give the percentage of maltose produced from damaged starch. The extrapolation is necessary to avoid the effect of variations in the rate of digestion of damaged starch from flour to flour.

S. M. MARSH

2635. **Total nitrogen in wheat. Dispersion of analytical results.** P. Navellier and J. Alegre (Lab. Municipal de Paris, France). *Ann. Falsif.*, 1960, **53**, 542–551.—Some indication is given of the size and sources of errors in sampling and reduction in the determination of total N in wheat by the Kjeldahl method. It is suggested that these errors account for the discrepancies found in N values from inter-laboratory trials.

B. J. WALBY

2636. **Rapid method for determining alpha-amylase activity.** S. Hagberg (Inst. Food Chem., Statens Hantverksinst., Stockholm, Sweden). *Cereal Chem.*, 1960, **37** (2), 218–222.—To a test-tube (21 mm × 220 mm) are added 5 g of flour, or finely powdered grain, and 25 ml of water, which are mixed by shaking for a standard time. A stirrer-viscometer (illustrated) is put into the mixture and the tube is immersed in a water bath at 100°, the surface of the mixture being 5 cm below the boiling-water level. Stirring is started 5 sec. after immersion of the tube in the bath. Two measurements are taken—(*i*) the gelatinisation time, that is, the time of heating required to produce a paste in which the stirrer-viscometer drops 70 mm in 0·25 sec. under its own weight; after the gelatinisation time has passed, the paste rapidly becomes thicker; (*ii*) the liquefaction time, that is, the total time of heating required to reduce the thick paste to a thin paste in which the stirrer-viscometer drops 70 mm in 1 sec. under its own weight. Then the diastatic number is (100 × 60)/(liquefaction time − gelatinisation time). The gelatinisation time for wheat flour was 25 to 40 sec. and, for rye flour, 20 to 35 sec. The liquefaction time ranges from < 30 sec. for wheat or rye flour of high amylase content to > 300 sec. for flour of low amylase content. Generally the liquefaction time is sufficient for the evaluation of the diastatic properties of any flour. It is shown that the diastatic number is linearly related to the α-amylase concn. The method is rapid, sensitive and reliable over a wide range of α-amylase concn., and requires simple apparatus.

D. B. PALMER

2637. **Separation and determination of sugar phosphates with particular reference to extracts of fish tissue.** N. R. Jones and J. R. Burt (D.S.I.R., Torry Res. Sta., Aberdeen, Gt. Britain). *Analyst*, 1960, **85**, 810–814.—The fish muscle (≃ 20 g) is homogenised with chilled $HClO_4$ (0·6N), the liquid is filtered at 0°, the pH of the filtrate is adjusted to 7 with 5N-KOH and, after 30 min., any pptd. $KClO_4$ is removed by filtration. The extract is run through a column of Dowex 1 (Cl^- form) and the column is washed with water until the extinction of the eluate at 260 mμ is < 0·01. The column, attached to an apparatus described, is eluted with a liquid in a gradient decreasing in $Na_2B_4O_7$ content and increasing in HCl and NaCl content, and 140 fractions are collected. The extinctions of the fractions are measured at 260 mμ to establish the positions of the nucleotide peaks. Aliquots (2 ml) from each fraction are withdrawn for the detection and determination of hexose and pentose phosphates by the anthrone test (Fairbarn, *Chem. & Ind.*, 1953, 86) and the orcinol test (Le Cage *et al.*, "Manometric Techniques and Tissue Metabolism", 2nd Ed., Burgen Publishing Co., Minneapolis, 1949, p. 185), respectively. The sharp appearance of material absorbing strongly at 260 mμ is a good indication that the elution of the monophosphate is complete.

A. O. JONES

2638. **Chemical composition of milk.** T. A. Nickerson (California Univ., Davis, U.S.A.). *J. Dairy Sci.*, 1960, **43** (5), 598–606.—Results for 28 milk components in 258 bulk samples from different areas are given and examined statistically in relation to variations with season, area, breed and feed. The significance of the results is discussed.

W. H. C. SHAW

2639. **The accuracy of the density method for the determination of solids-not-fat in milk.** K. F. Vogt and J. H. Labuschagne (Div. of Animal Husbandry and Dairying, Pretoria, S. Africa). *S. Afr. J. Agric. Sci.*, 1960, **3** (3), 395–402.—Samples (325) of milk taken between May 1958 and February 1959 were analysed for total solids (gravimetrically at 100°), fat (Gerber method with 10·77-ml pipette) and density (B.S. 734:1955). Mean values obtained, with their standard deviations, were—solids-not-fat, 8·593 ± 0·443%; fat, 3·929 ± 0·801%; density, 1·02808 ± 0·00118. A new multiple regression formula for determining s.n.f. from fat and density measurements was calculated and gave closer agreement between density and gravimetric methods than is obtained by either B.S.I. formulae (B.S. 734C:1959) or those of Roeder (*Milchwissenschaft*, 1953, **8**, 172).

This formula is—s.n.f. = 0·3158fat + 0·247d_{20} + 0·473. Tables are given for the 0·3158fat term and the (0·247d_{20} + 0·473) term. The mean difference between the values obtained with this formula and those obtained gravimetrically for s.n.f. was 0·098%, but this difference showed a seasonal variation and a standard deviation of 0·150.

J. I. M. JONES

2640. **Comparative accuracy of the plastic bead method of Golding and the lactometer method of Watson for routine determination of solids-not-fat in milk.** R. E. Erb, L. J. Manus and U. S. Ashworth (Washington State Univ., Pullman, U.S.A.). *J. Dairy Sci.*, 1960, **43** (5), 607–613.—An evaluation is made of a method in which plastic beads, graded in 10 density steps from 1·025 to 1·034, are used for the determination of s.n.f. in milk from the number of sunk beads, and results are compared with those calculated from lactometer readings. The plastic bead method is considered to be simple, rapid and sufficiently accurate for routine use.

W. H. C. SHAW

2641. **Composition of some New Zealand skimmed-milk powder and its influence on the determination of milk-solids-not-fat.** J. H. Halliday, E. H. W. J. Burden and J. J. Lamont (T. Wall & Sons Ltd., The Friary, Acton, London). *Analyst*, 1960, **85**, 839–840.—Use of the commonly accepted values of the Vieth ratio for ash, protein and anhydrous lactose (*viz*, 2:9:13) for calculating the non-fatty milk solids in ice-cream containing New Zealand skimmed-milk powder usually gave discordant results. Examination of 22 samples of such powder gave an average value for the ratio of non-fatty milk solids to anhydrous lactose to protein to ash of 25·25:11·55:10·40:2·05, and this ratio has been successfully applied to ice-cream containing New Zealand skimmed-milk powder. For a single sample of English spray-dried milk, the corresponding ratio was 24·8:12·2:9·8:2·0. Investigation showed that, in the evaporation of lactose soln. on the water bath, the lactose is present in the residue as the hydrated compound, and it is suggested that the term "non-fatty milk solids" should include the water of hydration of the lactose. The non-fatty milk solids in ice-cream containing New Zealand skimmed-milk powder is calculated by multiplying the anhydrous lactose content by 25·25/11·55 (*i.e.*, 2·18) or the protein content by 25·25/10·40 (*i.e.*, 2·43).

A. O. JONES

2642. **The accuracy of volumetric methods for the determination of fat in cheese.** K. F. Vogt and H. E. P. Köhler (Div. of Animal Husbandry and Dairying, Pretoria, S. Africa). *S. Afr. J. Agric. Sci.*, 1960, **3** (3), 403–408.—Comparisons were made on 73 cheese samples (Cheddar and Gouda) of the volumetric methods of van Gulik (Hermann, *Handbuch der landwirtschaftlichen Versuchs- und Untersuchingsmethoden*, Bd. 6, 2 Auflage, Neumann, Berlin, 1950), Babcock, and Gerber (British Standard 696: Part 2:1955) with the gravimetric method of Schmid and Bondzynski (SB). Only the Gerber method gave results not differing significantly from those obtained by the gravimetric method, the mean difference Gerber — SB being — 0·015% with a standard deviation of 0·215. It is recommended that the van Gulik and Babcock methods should not be used without modification, the former giving high results and the latter, low. More accurate butyrometers would give still better agreement.

J. I. M. JONES

2643. **Detection of lysolecithin in a sample of egg lecithin.** L. Saunders and J. Perrin (School of Pharmacy, Univ. of London, Brunswick Square, London, W.C.1). *J. Pharm. Pharmacol.*, 1960, **12** (Suppl.), 257T–259T.—Small quantities of lysolecithin protect a lecithin sol from flocculation by electrolytes to varying degrees. The presence of lysolecithin can be detected and its amount (< 4%) can be determined by measurement of the turbidity of the flocculated sol. *Procedure*—Mix equal volumes of a 0·1% phosphatide sol and 0·01M-KCl, set aside for 2 hr. and measure the extinction in a 0·5-cm cell with a Hilger 605 filter.

A. R. ROGERS

2644. **Detection of artificial organic colouring matters in orange peel.** H. Suter and H. Hadorn (Lab. VSK, Basel, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1960, **51** (4), 293–303.—Artificial colourings cannot be separated satisfactorily from the natural carotenoids by paper chromatography, and the method described is based on adsorption chromatography on Al_2O_3 with fractional elution. The isolated colourings can then be identified by paper chromatography and by determination of their absorption spectra. *Procedure*—Extract 10 g of dried peel with light petroleum for 4 hr., distil off the solvent and dissolve the residue in 10 ml of methanol and 10 ml of ether; then saponify with 3 ml of 25% methanolic KOH. Filter and add 25 ml of water. Separate the aq. phase and extract with 5 ml of ether, wash the ether extracts with water and distil off the ether after drying with Na_2SO_4. Wash the residue into a separating-funnel with 15 ml of light petroleum and extract with 15 ml of methanol (90%) and separate the two layers. Evaporate the light petroleum extract and re-dissolve the residue in 2·5 ml of light petroleum. Add 20 ml of water and 20 ml of ether to the methanol phase and shake. Dry the ether layer with Na_2SO_4, evaporate and dissolve the residue in 2·5 ml of light petroleum. Chromatograph the two extracts on a column of Al_2O_3 (described) and elute with a series of solvents (listed).

I. DICKINSON

2645. **Spectrophotometric determination of sorbic acid in butter and margarine.** L. Laporta (Lab. Chim. Prov., Pescara, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (3, Suppl.), 649–666.—A review of published methods is given, and the following improved method is presented. *Procedure*—Homogenise the sample (30 to 40 g) and transfer an accurately weighed amount (≃ 1 g) to a 500-ml distillation flask containing $MgSO_4.7H_2O$ (200 g). Add a few pieces of pumice and 0·1M-H_2SO_4 (200 ml), and distil till the residue in the flask solidifies. To the distillate (≃ 190 ml) add N-HCl (2 ml) and make up to 200 ml. Measure the extinction in a 1-cm cell at 263 mμ against 0·01N-HCl. Carry out a control similarly with butter or margarine free from sorbic acid, and subtract the extinction of the control from that of the sample to give the net extinction, which, for butter, is divided by 1·165 to give mg of sorbic acid. For margarine the net extinction is reduced by 0·010 before calculation. Mean recoveries were ≃ 95·5%.

J. I. M. JONES

2646. **Investigation into the use of bioassay for pesticide residues in foodstuffs. Report to the Analytical Methods Committee of The Society for Analytical Chemistry.** P. H. Needham. *Analyst*, 1960, **85**, 792–809.—The methods employed in a

number of British and European laboratories are reviewed. The techniques employed may be divided into three types—(*a*), direct methods in which the test organisms are confined over a pulp of the sample containing the residue; (*b*), film methods in which the test organism is exposed to the residue after its extraction from the sample; and (*c*), aqueous methods in which the residue, after extraction from the sample, is added to water containing an aquatic organism. Applications of these types of procedure are described. (98 references.) A. O. JONES

2647. **Application of the total organic chlorine method to the determination of endrin and thiodan residues in blackcurrants.** H. Egan and W. H. Evans (D.S.I.R., Lab. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1960, **85**, 842–843.—An earlier method (Sergeant, *Ibid.*, 1958, **83**, 335; Sergeant and Thompson, *Ibid.*, 1959, **84**, 251) has been applied directly to the determination of endrin in blackcurrants. Recoveries of 0·98 p.p.m. were 97%, but with lower amounts (0·49 p.p.m.) the recovery was 72%. For thiodan the method is modified in that separation of thiodan from thiodan alcohol and from interfering substances is achieved by elution from activated alumina with benzene in place of hexane. The sample of blackcurrants (100 g) is extracted with a mixture of 100 ml each of acetone and hexane or light petroleum. The washed extract is concentrated to $\simeq$ 1 ml of hexane as previously described (*loc. cit.*), applied to the alumina column (prep. described) and washed in with 10 ml of benzene, the first 10 ml of eluate being discarded. Elution is continued at 2·0 to 2·5 ml per min., another 20 ml of benzene being added to the column, and the next 20-ml fraction being collected. Liquid paraffin (2 drops) is added to the fraction and the benzene is removed by evaporation in a stream of dry air at 40°. The total organic chlorine is then determined (*loc. cit.*).
A. O. JONES

2648. **Analysis of beverages based on orange juice.** C. Damiani (Lab. Chim. Prov., Milano, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (3, Suppl.), 608–619.—The analysis of orange juice and beverages prepared therefrom, based on formol titration and the chromatographic identification of amino-acids, is investigated, and it is concluded that these methods are unreliable as indices of quality or genuineness. J. I. M. JONES

2649. **Methods for distinguishing grades of olive oil in mixtures.** G. Jacini, G. de Zotti, P. Capella and A. Arpino (Stazione Sper. Olii e Grassi, Milan, Italy). *Olii Min.*, 1960, **37** (10), 419–427.—Methods for distinguishing between virgin, refined, second pressing and extracted olive oil in mixtures are discussed. These include u.v. spectrophotometry at 240 to 290 mμ, column chromatography on silica gel (together with paper chromatography for sterols), i.r. spectrophotometry, especially at 10·36 mμ, and the iodine value of the solid fatty acids. These methods are compared, and a general procedure is given. C. A. FINCH

2650. **Application of ultra-violet spectrophotometric analysis in the control of olive oil.** B. Doro, V. Sadini and G. Gabucci (Lab. Chim. Prov., Trieste, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (3, Suppl.), 499–535.—Chemical and physical constants are not adequate to determine the quality of olive oil, and judgements based thereon are liable to over-rate the quality; thus, of 88 reputed virgin oils, only 76% were shown to be genuine, the remaining 24% being mixtures with solvent-extracted oils. Only u.v. spectrophotometry enables certainty in grading to be achieved. The formula of Spiteri (*Inform. Oleic. Intern.*, 1958, **94**, Apr.–May–June) is used in addition to the usual chemical constants. The value $K'_{268} = K_{268} - (0{\cdot}023 \times \text{acidity})$ is calculated, where K_{268} is the extinction at 268 mμ and the acidity is expressed as oleic acid (%). Oils for which K'_{268} is $< 0{\cdot}17$ are genuine virgin oils; those for which K_{268} is $> 0{\cdot}11$ have K'_{268} values $> 0{\cdot}17$ and are abnormal or adulterated, abnormality arising possibly from faulty handling or storage. Ultra-violet spectrophotometric characteristics, and formulae suggested by other workers, are reviewed and criticised, and analytical constants, spectrophotometric and organoleptic data and quality classifications are given for 200 samples.
J. I. M. JONES

2651. **The investigation of alkaline impurities in olive oil. A new method of identification of virgin olive oils.** A. Romeo, R. Cuzzocrea and E. Foti (Lab. Chim. Prov., Reggio, Calabria, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (3, Suppl.), 536–545.—Two methods, based on the determination of alkaline substances (soaps) are suggested for distinguishing between virgin and refined olive oils. *Procedures*: (*i*) *Bromophenol blue titration*—Stir the oil (10 ml) vigorously with bromophenol blue reagent (10 ml) for 1 min. After separation of the layers, titrate with 0·005N-H_2SO_4 in 96% ethanol, added dropwise on to the surface till the original colour of the reagent is restored. Prepare the reagent by diluting a 0·4% soln. of bromophenol blue in 90% ethanol (10 ml) to 1 litre with 96% ethanol and adjusting to pH 4·0 with 0·005N-ethanolic H_2SO_4, with a glass electrode. In studies with known virgin oils and commercial refined oils, the former showed a proportionality between the acidity and the bromophenol blue figure up to 4% of oleic acid (which is a proposed statutory criterion for virgin oils); when the acidity was plotted against the bromophenol blue figure as abscissa, the points for the virgin oils all lay on the left side of a line connecting the points for an oil of $\simeq$ 4% acidity and one of $\simeq$ 1% acidity, while those for refined oils lay on the other side. (*ii*) *Conductivity measurements in acetone soln.*—Add the oil (10 g) to anhydrous acetone of zero conductivity (50 ml) and measure the conductivity at 20°. Then add H_2O from a micro-burette to the point of incipient turbidity and re-measure the conductivity. The temperature-correction factor for conductivity determined experimentally is 0·025 per °C. The same oils as in (*i*) were studied; H_2O additions ranged from 0·7 to 1·5 ml. Known virgin oils with acidity up to 3% showed zero conductivity without and with H_2O; those with 3 to 4% acidity showed zero conductivity without and < 1 μmho per cm with H_2O. Refined oils showed high conductivity without or with H_2O. It is suggested that zero conductivity without H_2O, and a maximum of 1·1 μmho per cm with H_2O, should be specified as criteria for virgin oils of acidity up to 4% as oleic acid. J. I. M. JONES

2652. **Quantitative determination and study of iso-oleic acid during the hydrogenation of sunflower-seed oil by paper chromatography. I. Optical evaluation with a micro-photometer.** V.

Koman and E. Komanová (Dept. Tech. Microbiol. and Biochem., Inst. Chem. Tech., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (10), 690–700.—Chromatography was carried out on Whatman No. 1 paper impregnated with light petroleum of boiling-range 190° to 220°. The fatty acids were separated by developing for 5 hr. at 25° with acetone - acetic acid - H_2O (8:1:2) saturated with undecane, or for 12 hr. at — 30° with acetone - propionic acid - H_2O (8:6:1). The separated fatty acids were detected with dithio-oxamide after conversion into copper salts. The unsaturated fatty acids were detected with 1% $KMnO_4$ soln. The quantitative evaluation of the spots was carried out photographically with a Keramos F–3 spectrophotometer and comparison with a standard of oleic acid. The error was $\pm$ 4·3%.

J. Zýka

2653. **Determination of small proportions of linolenic acid in vegetable oils by alkaline isomerisation.** J. G. Nørby (Biokem. Inst., Århus Univ., Denmark). *Acta Chem. Scand.*, 1960, **14** (9), 2057–2059 (in English).—Small proportions of trienoic acid are determined by the micro-isomerisation method of Herb and Riemenschneider (*Brit. Abstr. C*, 1953, 426) and the method of calculation due to Brice and Swain (*J. Opt. Soc. Amer.*, 1945, **35**, 532). A sample wt. of 1 to 20 mg is used, and equations are given for the calculation of the corrections for background absorption under various conditions, so that the trienoic acid content can be derived from the u.v. spectra of the oil before and after isomerisation. C. S. Howes

2654. **Identification and determination of *p*-dimethylaminoazobenzene (DAB) in adulterated oils.** E. Rogliani, D. Cozzolino and V. Capano (Ist. Chim. Biol., Univ. Napoli, Italy). *Biochim. Appl.*, 1960, **7** (4), 187–192.—The adulterated oil (20 ml) is extracted with 20% HCl (3 × 25 ml) and the combined extracts are adjusted to pH 3·5 with 2N-NaOH. A few strands of white wool, degreased with ether, are placed in the soln., which is gently warmed till decolorised. The wool is then washed well with slightly acidified H_2O and the colour is extracted with several 5-ml portions of light petroleum. The combined extracts are evaporated to small vol., made up to 1 ml with light petroleum and subjected to descending chromatography on Whatman No. 1 paper with butanol - pyridine - H_2O (29:21:15) for 24 hr. A control is run with pure DAB in light petroleum. The R_F value is 0·91 and the minimum quantity detectable is about 40 μg. Under the same conditions, *p*-aminoazobenzene (Aniline yellow) has an R_F value of 0·79. For quant. determination the spot is cut out and eluted with light petroleum, and the extinction is measured at 420 mμ, submitting a standard of pure DAB in olive oil to the same procedure. If no other colouring matter is present, the determination can be made directly on the light petroleum extract from the wool, or on a 20% HCl extract of this extract, in which case the colour is pink and the extinction is measured at 540 mμ. The extinction *vs.* concn. curve is linear for 25 to 150 μg of DAB per 5 ml in light petroleum and for 20 to 100 μg per 5 ml in the HCl extract. J. I. M. Jones

2655. **Microchemical determination of the peroxide value and susceptibility to rancidity of oils.** P. Mario and G. Istrana (Ist. Tecnol. Aliment., Roma). *Olii Min.*, 1960, **37** (10), 441–446.—A colorimetric microchemical method for determining the peroxide value of oils is described, in which the oil in acetone soln. is loaded on to a paper, which is developed with 10% NH_4SCN soln. containing 0·5 ml of conc. H_2SO_4 and 5 g of $FeSO_4.7H_2O$ per 50 ml of water. The direct relationship between this method and those of Schaal and of Täufel and Vogel is demonstrated. C. A. Finch

2656. **Complexometric determination of antioxidants. III. Semi-micro determination of butylated hydroxyanisole in lard and separation from nordihydroguaiaretic acid.** B. A. J. Sedláček (Inst. for Nutrition Res., Prague, Czechoslovakia). *Fette, Seif., Anstrichmitt.*, 1960, **62** (11), 1041–1044.—The complexometric method for the determination of nordihydroguaiaretic acid (NDGA) in lard (*Anal. Abstr.*, 1961, **8**, 1235), which is based on the determination of the Ag formed by reaction with buffered $AgNO_3$ soln., has been modified for the determination of butylated hydroxyanisole (BHA). The extraction of BHA from a soln. of lard in light petroleum is carried out with 76% ethanol instead of 50% methanol from larger samples (containing 4 mg of BHA), and the soln. used are 0·002M instead of 0·005M. A method for the separation of NDGA and BHA from a single sample of lard is described which involves successive extraction with 50% methanol (for NDGA) and 76% ethanol (for BHA). Methods of calculation are detailed and the comparative accuracy of the methods is discussed.

S. M. Marsh

2657. **Use of *ortho*-phthalic - ethylene glycol polyester in gas - liquid chromatographic analysis of fatty acid esters.** B. M. Craig (Prairie Reg. Lab., Nat. Res. Council, Saskatoon, Saskatchewan, Canada). *Chem. & Ind.*, 1960, (47), 1442.—The polyester of *o*-phthalic acid with polyoxyethylene glycol has been prepared (*cf.* Fischer, *J. Polym. Sci.*, 1960, **44**, 155) and found to be effective in the gas-chromatographic separation of the methyl esters of fatty acids. N. E.

2658. **Estimation of riboflavine by a.c. polarography.** B. Breyer and T. Biegler (Section of Agric. Chem., Dept. of Agric., Univ., Sydney, Australia). *J. Electroanal. Chem.*, 1960, **1** (6), 453–457 (in English).—The a.c. polarographic technique previously described (Breyer *et al.*, *Aust. J. Sci. Res., Ser. A*, 1950, **3**, 558) is applied to the determination of riboflavine (**I**). Under these conditions, **I** gives a wave down to 2×10^{-7}M (the lower limit under d.c. conditions is 5×10^{-6}M). Calibration curves were linear up to $\simeq 3 \times 10^{-5}$M, according to the pH. The optimum range for analysis (error $\simeq$ 2%) was 10^{-6}M to 10^{-5}M, currents then being in the range 1 to 10 μA (r.m.s.). Greater errors ($\simeq$ 10%) at lower concn. are due partly to instrumental factors and partly to base-line construction difficulties. For max. stability of **I**, the determination is best carried out in buffers at pH 4 to 5. Pharmaceutical products are extracted with H_2O, an aliquot is added to acetate buffer (pH 4·7) and the wave height at — 0·35 V *vs.* the S.C.E. is measured; O need not be removed. With milk, a borate buffer is used. *Procedure with milk*—Treat the sample (10 ml) with M-$HClO_4$ (1 ml) to precipitate casein, and centrifuge. Add the supernatant liquid (5 ml) to borate buffer (pH 9·5) (10 ml) and measure the **I** wave at — 0·48 V. Repeat with a sample of milk to which standard **I** soln. (2×10^{-4}M) (0·15 ml) has been added and measure the increase in wave height. G. Russell

2659. **Amperometric determination of ascorbic acid with chloramine T.** G. S. Deshmukh and M. C. Eshwar (Div. Anal. Chem., Hindu Univ., Benares). *J. Sci. Ind. Res., India, B*, 1960, **19** (12), 502–503.—A study of different oxidising agents, including NaOBr, for the electrometric determination of ascorbic acid showed that an aq. soln. of chloramine T gave encouraging results. *Procedure*—A simple form of amperometric unit, (Kolthoff *et al., Analyst*, 1953, **78**, 405) with a rotating platinum-wire micro-electrode is used. Aliquots of ascorbic acid soln. (≃ 0·2N, standardised with KIO_3) are added to a buffer mixture of citric acid (0·2M) (10 ml) and Na citrate (0·2M) (10 ml) at pH 4·0 to 4·5. After dilution to 50 ml with H_2O, the mixture is titrated at + 0·3 V *vs.* the S.C.E. with chloramine T soln. (≃ 0·1N, standardised iodimetrically) without de-aeration. The difference between the ascorbic acid taken and that found varied, in 8 determinations, between + 0·366 and − 0·875%. I. A. SIMPSON

2660. **Variation of the area of L-ascorbic acid spots on paper chromatograms.** K. Bogdański, J. Jeszka and M. Kenner (Dept. of Food and Vitamin Technology, Polytechnic, Łódź, Poland). *Chem. Anal., Warsaw*, 1960, **5** (5), 781–789.—Factors such as the concn. of the ascorbic acid soln., the composition of the solvent system, the kind of paper used and the technique for placing the sample on the paper are investigated and the results are statistically examined. The area of the spot per unit of wt. decreases with increase in concn. of the test soln. To obtain satisfactory results it is necessary to perform at least 5 determinations of test and standard soln. under identical conditions. B. K.

See also Abstracts—**2469**, Determination of reducing sugars. **2471**, Separation of sugars. **2538**, Wet-oxidation procedure. **2549**, Arsenic in biol. materials. **2557**, Ascorbic acid in urine. **2558**, Nicotinic acid assay. **2613**, Panthenol assay. **2616**, Determination of allyl isothiocyanate.

Sanitation

2661. **Field test for nitrobenzene vapour in air.** G. C. Hands (D.S.I.R., Lab. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1960, **85**, 843–845.—A 6-litre sample of the air to be tested is drawn through 2 ml of 2-ethoxyethanol in a bubbler. Zinc amalgam (1 ml) and 4 ml of HCl are added and the mixture is shaken. The aq. layer (5 ml) is transferred to a dry tube, 0·5 ml of $NaNO_2$ soln. (3·5%, w/v) is added and, after 2 min., 2 ml of Na_2CO_3 soln. and then immediately 0·5 ml of R salt (Na 2-naphthol-3,6-disulphonate) soln. (0·8% of the sodium salt adjusted to pH 8 with Na_2CO_3). Finally dil. aq. NH_3 is added and the colour is compared with that of standards prepared from soln. of $K_2Cr_2O_7$ and $CoSO_4$. The method can be used for determining concn. of 0·5 to 2·0 p.p.m. (v/v) of nitrobenzene and for concn. outside these limits by increasing or decreasing the size of the sample. A. O. JONES

2662. **Determining suspended solids [in sewage] using a spectrophotometer.** D. Krawczyk and N. Gonglewski (Buffalo Sewer Authority, Buffalo, N.Y., U.S.A.). *Wat. & Sewage Wks, Reference No.*, 1960, R91–R94.—A rapid method is described. Correlation of results with those by the Gooch crucible method is good, and the standard deviation is less. The sample (diluted if necessary) is mixed in a blender for exactly 1·5 min. and the transmittancy (T) of a 25-ml aliquot is measured at 10,000 A against a water blank. The curve of concn. of suspended solids *vs.* T is linear for values of T between 30 and 90%. S. C. I. ABSTR.

2663. **Suggested modified method for colorimetric determination of selenium in natural water.** G. B. Magin, jun., L. L. Thatcher, S. Rettig and H. Levine (U.S. Geol. Survey, Washington, D.C., U.S.A.). *J. Amer. Wat. Wks Ass.*, 1960, **52** (9), 1199–1205.—Up to 50 μg of Se in natural water can be determined spectrophotometrically, with mannitol - 3,3′-diaminobenzidine hydrochloride as reagent. This forms a piazselenole which is quantitatively extracted with toluene at pH 6 to 7. EDTA is used to minimise interference. The precision is ± 1 μg. This method cannot be used satisfactorily with brines. E. M. MAYES

2664. **Colorimetric determination of chlorates in well waters.** P. Urone and E. Bonde (Dept. of Chem., Univ. of Colorado, Boulder, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1666–1668.—The reaction of ClO_3^- with Cl^- in acid soln. to yield Cl is used to produce a colour with *o*-tolidine. *Reagents*—For the *o*-tolidine soln., dissolve 0·4 g of *o*-tolidine dihydrochloride in 400 ml of H_2O; add 250 ml of conc. HCl, cool, and dilute to 1 litre. For the chlorate standards, dissolve 1·2755 g of $NaClO_3$ in 1 litre of water (1 ml ≡ 1 mg of ClO_3^-); dilute this to the required concn., *e.g.*, 0·005 mg of ClO_3^- per ml. *Procedure*—To the sample (4 ml) add *o*-tolidine soln. (1 ml) and mix rapidly, then stir in conc. HCl (5 ml). A yellow colour develops if ClO_3^- are present. After 5 min. and before 30 min. measure the extinction of the soln. with a spectrophotometer at 448 mμ for low, and at 490 mμ for high, concn. of ClO_3^-. Calibrate by using a suitable aliquot of standard soln. diluted to 4 ml. Free Cl and Fe^{3+} interfere, but simple correction factors can be applied; NO_3^- interfere, but there is no interference from Cl^- or NO_2^-. The system follows Beer's law closely except at low concn. The acid concn. of the soln. should be > 6N. Concn. of ClO_3^- from 0·05 to 10 p.p.m. are measured with an average deviation of 0·02 p.p.m. Higher or lower concn. may also be measured. H. A. FONER

2665. **Chromatographic analysis of phenols in effluent water from the low-temperature carbonisation and from high-pressure gasification of coal.** L. Barker and N. W. Hollingworth (Houldsworth Sch. of Appl. Sci., Univ. Leeds, England). *Chem. Průmysl*, 1960, **10** (10), 525–528.—The chromatographic separation was carried out on two columns with different stationary phases. The columns contained Celite 535 as carrier; 0·1N-HCl was used as stationary phase for the first column and a 5% soln. of sodium silicate for the second. Sulphites were removed from the sample by acidification with HCl, and 1 ml of the clear liquid was mixed with 2 g of Celite and transferred to the column with the acid stationary phase. With cyclohexanone as eluent all monohydric phenols are eluted together, but phenol forms a separate zone. The addition of n-butanol to the cyclohexanone permits the elution of the dihydric phenols. Monohydric

phenols (cresols and a part of the xylenols) are then separated on the second column. The separated phenols are determined by u.v. spectrophotometry. J. ŽÝKA

See also Abstracts—**2311**, ^{90}Sr in water. **2320**, B in sea water. **2386**, Thiosulphate in effluents.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

2666. **Sampling studies of sugar cane for juice analysis.** S. C. Sen (Central Sugarcane Res. Inst., Pusa, India). *Int. Sugar J.*, 1961, **63** (1), 3–4.—From the results of analysis for pol content on each clump on 72 plots of 1/80 acre it is calculated that ten whole clumps taken at random on plots of this size will give a reliable estimate of pol content. N. E.

2667. **Rapid determination of nitrate and nitrite in plant material.** J. T. Woolley, G. F. Hicks and R. H. Hageman (Soil and Water Conservation Res. Div., Agric. Res. Serv., U.S. Dept. Agric., Univ. Illinois, Urbana). *J. Agric. Food Chem.*, 1960, **8** (6), 481–482.—The method of Nelson *et al.* (*Anal. Abstr.*, 1954, **1**, 2386) for determining nitrate and nitrite in plant material is improved by using a trace of Cu in the reduction of nitrate to nitrite, by adding rather more of the reagent powder, and by allowing more latitude in the time schedule. M. D. ANDERSON

2668. **Analysis of seed disinfectants based on phenylmercuricatechol.** G. Rentsch (Pharmakol. Inst., Med. Akad., Magdeburg, Germany). *Z. anal. Chem.*, 1960, **178** (2), 100–103 (in German).—The reaction of phenylmercuricatechol (**I**) with 4-aminophenazone (**II**) forms the basis of the method. X-ray analyses of pure and adulterated **I** are compared. *Procedure*—Shake 10 g of the sample with 1% NaOH soln. (50 ml) for 30 min. and filter. Add activated charcoal, shake and re-filter. Remove coloured matter by passing the soln. through Al_2O_3, and other interfering elements with Dowex-50 resin (H^+ form). Shake the eluate with ether to remove catechol (**III**) and take a small aliquot (containing 2 to 100 μg of **I**) from the aq. phase. Add 4 ml of 0·2M-Sörensen phosphate buffer (pH 7·6), 0·5 ml of acetone, 0·3 ml of a 2% aq. soln. of **II** and 0·5 ml of 2% aq. $K_3Fe(CN)_6$ soln. Measure the extinction after 8 to 12 min. at 560 mμ *vs.* a reagent blank. Paper chromatography can also be used to separate **I** and **III**; phenylmercury acetate does not interfere.
P. D. PARR-RICHARD

2669. **Ultra-violet method for determination of streptomycin in feeds.** S. E. Katz (Dept. Agric. Chem., New Jersey Agric. Exp. Sta., New Brunswick, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (6), 501–503.—Streptomycin is extracted from feeding-stuffs by 0·02N-H_2SO_4; the extract is centrifuged, filtered and neutralised; the ppt. is removed by centrifuging and filtering. The filtrate is chromatographed on Amberlite IRC-50 (Na^+ form), and the streptomycin is eluted with 2% H_2SO_4; the streptose part of the molecule is then converted by alkali into maltol; the extinction of the soln. is measured at 324 mμ before and after conversion, and the difference is compared with a standard curve. This method is more sensitive than the colorimetric method for maltol. Recoveries of streptomycin from poultry feed were 75 to 108%.
M. D. ANDERSON

2670. **Determination of furazolidone and nitrofurazone in chicken tissues.** R. J. Herrett and J. A. Buzard (Eaton Laboratories, The Norwich Pharmacal Co., Norwich, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1676–1678.—Procedures are given for the extraction of the nitrofuraldehyde derivatives from chicken tissues by treatment with dil. HPO_3, and for the formation, and separation on an alumina column, of 5-nitro-2-furaldehyde phenylhydrazone. The phenylhydrazone is determined by its extinction in toluene soln. at 440 mμ. Good recoveries have been obtained from chicken liver, muscle and fat containing 1 to 5 p.p.m. of either of the nitrofuraldehyde derivatives.
R. M. ROWLEY

2671. **Rapid polarographic determination of pentachloronitrobenzene on forage and comparison with a spectrophotometric method.** C. A. Bache and D. J. Lisk (Pesticide Residue Lab., Dept. of Entomology, N.Y. State Coll. Agric., Cornell Univ., Ithaca, N.Y.). *J. Agric. Food Chem.*, 1960, **8** (6), 459–460.—The fungicide pentachloronitrobenzene is extracted from forage by tumbling with Skellysolve B, filtering and drying the extract, and removing interfering substances by adsorption on Attaclay, freezing, and chromatography on Florisil; the solvent is then evaporated, the residue is dissolved in isopropyl alcohol with Na acetate and acetic acid as supporting electrolyte, and, after de-oxygenation, the polarogram is recorded from 0 to − 1·15 V *vs.* the S.C.E. Recovery of fungicide from forage was 76 to 130%. Results agreed well with those obtained by the spectrophotometric method of Ackermann *et al.* (*Anal. Abstr.*, 1959, **6**, 3262). M. D. ANDERSON

2672. **Determination by gas-phase chromatography of 2-methylphenoxyacetic, 2-methylphenoxypropionic and 2-methylphenoxybutyric acids, and their 4- and 6-chloro-derivatives and 4,6-dichloro-derivatives.** F. Martin, S. Vertalier and J. Camier (Soc. des Usines Chim. Rhône-Poulenc, Lab. de Rech. Anal., Vitry-sur-Seine). *Bull. Soc. Chim. France*, 1960, (11–12), 2067–2071.—A method is described for the separation of the substituted phenoxy-acids encountered in selective weed-killers. Two isolation techniques by acidification with HCl and extraction with ether are described, and a supplementary extraction with $NaHCO_3$ is advocated if much cresol is present. Before transference to the gas chromatograph the acids are esterified with diazomethane. Alternative liquid phases, carried on Sil-O-Cel C22, are silicone oil and poly(diethylene glycol) succinate, and hydrogen at 215° to 220° is used as carrier gas. Both methyl adipate and phenyl benzoate are used as internal standards. Either of the liquid phases can be used to separate members of a single family. The use of poly(diethylene glycol) succinate permits the complete separation of mixtures containing the acetic and propionic acids. Mixtures of either acetic or propionic derivatives with butyric derivatives must be examined successively on the two liquid phases, as also must mixtures of the three groups. J. R. HUDSON

2673. **Chromato - polarographic investigations. XIV. Separation and quantitative evaluation of DDT isomers.** W. Kemuła and A. Krzemińska (Dept. of Inorg. Chem., Univ., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (4), 611–616.—A soln. of DDT (≃ 0·02M) in aq. dimethylformamide (87%) containing tetraethylammonium iodide (0·05M) is passed through a powdered rubber - n-heptane (1:1) column, and the *pp'*- and *op'*-isomers are determined in appropriate fractions of the percolate by "polarographic integration" (*cf. Ibid.*, 1956, **1**, 36). Although, owing to instability, a fresh column is required for each determination, results were within ± 5%, and the time required (4 hr.) compares favourably with kinetic methods. P. Brych

2674. **Determination of heptachlor and heptachlor epoxide in soil.** R. T. Murphy and W. F. Barthel (Plant Pest Control Div., Agric. Res. Serv., U.S. Dept. Agric., Gulfport, Mo.). *J. Agric. Food Chem.*, 1960, **8** (6), 442–445.—In the method described for determining heptachlor (**I**) and heptachlor epoxide, a larger sample is used than in previous methods to improve sensitivity. A plot is sampled by taking 50 cores diagonally across it with a 2-in.-diameter auger set for a 2-in. depth, and by using the upper 1 in. of each core. From the mixed cores, 500 g of (unheated) soil is taken, and extracted with pentane - isopropyl alcohol (3:1). The extract (500 ml) is concentrated to 250 ml, freed from isopropyl alcohol by washing with water, dried over Na_2SO_4, treated with fuming H_2SO_4, washed with water, dried again, and chromatographed on columns of Florisil and carbon, eluting **I** with 2% benzene in pentane, and the epoxide with a 5% soln. of ether in pentane. After removal of most of the solvent, the substances are determined from extinctions at 567 mμ and 410 mμ, and comparison with standard curves. The lowest concn. of insecticide that could be accurately determined was 0·01 p.p.m. A rapid loss of **I** occurs immediately after application to soil, after which there is very little loss, even in warm weather; some **I** is converted into the epoxide.

M. D. Anderson

2675. **Colorimetric estimation of dodecylguanidine acetate residues.** W. A. Steller, K. Klotsas, E. J. Kuchar and M. V. Norris (Cent. Res. Div., American Cyanamid Co., Stamford, Conn., U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (6), 460–464.—The fungicide n-dodecylguanidine acetate is determined by forming the complex with the anionic dye bromocresol purple in buffered aq. ethanol, extracting the complex into $CHCl_3$, shaking with aq. alkali (which extracts an amount of bromocresol purple equivalent to the fungicide), measuring the extinction of the extract at 590 mμ, and comparing with calibration curves. The method is applicable to residues of 0·2 to 0·6 p.p.m. in a 50-g sample. Surface residues are separated by tumbling with methanol, and total residues by macerating with methanol - $CHCl_3$ (2:1). Determinations on apples, apple leaves and cherries are reported.

M. D. Anderson

2676. **Colorimetric determination of halogenated nitrophenols added to streams as sea-lamprey larvicides.** M. A. Smith, V. C. Applegate and B. G. H. Johnson (Bucknell Univ., Lewisburg, Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1670–1675.—The determination of 4-nitro-3-trifluoromethylphenol in alkaline soln. at 395 mμ is complicated by the natural colour of the stream-water. However, the extinction of the water at pH 9 is proportional to the extinction at pH 3, and the extinction of the nitrophenol is negligible at pH 3, so that a correction can be made. The average error for 12 determinations in the range 2 to 6 p.p.m. was 0·1 p.p.m.; the greatest error was 0·2 p.p.m. R. M. Rowley

---

See also Abstracts—**2646**, Bioassay of pesticide residues. **2647**, Endrin and thiodan.

5.—GENERAL TECHNIQUE AND APPARATUS

General

2677. **Automatic physical analytical apparatus for the laboratory and chemical works.** E. Krell. *Chem. Tech., Berlin*, 1960, **12** (10), 575–580.—A review is presented of the apparatus and methods developed in Germany and other countries for effecting automatic continuous analyses in a wide variety of chemical and allied fields, including spectrometry, chromatography, electrophoresis and fractionation. The possibilities of extending automation in analysis are discussed.

H. L. Whitehead

2678. **A modification of Consden's desalting apparatus.** J. Gardner (Agric. Res. Council, Field Station, Compton, Berks., England). *J. Med. Lab. Technol.*, 1960, **17** (4), 241–243.—The desalting apparatus of Consden *et al.* (*Biochem. J.*, 1947, **41**, 590) has been modified by the replacement of the mercury - water separator with a longer column, which both removes ions from the mercury more efficiently and prevents the mercury carrying any water into the anode chamber. Details for the construction of the mercury washer and separator are given. R. A. Brenan

2679. **A micro ultrafiltration apparatus.** R. H. Wilkinson (Hospital for Sick Children, Great Ormond Street, London, W.C.1). *J. Clin. Path.*, 1960, **13** (3), 268–270.—The apparatus described can be used for the ultrafiltration of 0·2 to 1·0 ml of body fluids. It consists of two flanged glass tubes held together by a brass clamp; Cellophane P.T. 600 is placed between the flanges and pressure is applied by means of mercury and a reservoir.

R. A. Brenan

2680. **Thermogravimetric measurements.** A. E. Newkirk (General Electric Res. Lab., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1558–1563.—Errors and limitations not generally recognised are discussed. Only thermobalances in which the sample is exposed to gases at a pressure approximating to 1 atm. are considered. The importance of the performance of blank runs on inert samples is emphasised, and attention is drawn to errors in recorded temperature incurred when there is a possibility of a thermal lag or a finite reaction time.

E. G. Cummins

2681. **A convenient system of thermogravimetric analysis and of differential thermal analysis.** M. M. Markowitz and D. A. Boryta (Res. and Dev. Lab., Chemicals Div., Foote Mineral Co., Berwyn, Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1588–1592.—

A new apparatus suitable for thermogravimetric and differential thermal analysis is described. Differential thermal analysis curves for K_2SO_4, $(LiPO_3)_n$ (crystalline) and $(LiPO_3)_n$ glass are given.
E. G. CUMMINS

2682. **Differential thermal analysis by the dynamic gas technique.** R. L. Stone (R. L. Stone Co., 3314 Westhill Drive, Austin 4, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1582–1588.—The apparatus described has been developed so that the pressure and temperature of the system, as well as the composition of the gas flowing through test powders during an experiment, may be under control. Thermograms illustrate the effect of changing one of these variables at a time. The importance of inflections in original, untouched thermograms is emphasised. E. G. CUMMINS

2683. **Thermogravimetry in self-generated atmospheres.** P. D. Garn and J. E. Kessler (Bell Telephone Lab., Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1563–1565.—This modification of technique, which simply involves the use of a cylindrical porcelain sample-holder, improves the definition of thermogravimetric curves. The aim is to provide an atmosphere of evolved gas at $\simeq$ 1 atm. pressure.
E. G. CUMMINS

2684. **Differential thermal analysis of epoxide reactions.** H. C. Anderson (Non-metallic Materials Div., U.S. Naval Ordance Lab., Silver Spring, Md., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1592–1595.—Studies of six epoxides have shown that the temperatures at which each system undergoes endo- or exo-thermic reaction are characteristic properties of that system, and that the resulting thermograms can be used as a characterisation index. E. G. CUMMINS

2685. **Isobaric dissociation studies of alkali-metal carbonate hydrates using simultaneous differential thermal analysis - thermogravimetric analysis.** A. Reisman (Watson Lab., Internat. Business Machines, 612 West 115th St., New York, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1566–1574.—The applicability of differential thermal analysis, thermogravimetric analysis and X-ray methods, and a combined approach, in which the first two techniques are used to measure the thermal and mass properties of a single sample simultaneously, is discussed. In addition, experimental equipment suitable for performing isovolumic experiments in the temperature interval $-190°$ to $+400°$ is described. Results obtained by the use of this equipment are presented in support of conclusions reached on the basis of isobaric experiments. It is concluded that polyhydrate systems may not be readily definable when the isobaric approach alone is employed. E. G. CUMMINS

2686. **Zone melting and differential thermal analysis of some organic compounds.** M. J. Joncich and D. R. Bailey (Dept. of Chem., Univ. of Tennessee, Knoxville, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1578–1581.—Details are given of the construction of an 18-zone apparatus, consisting of a borosilicate-glass tube (20 mm external diam.) surrounded with alternate cold and hot regions (18 heated regions 14 mm long, and 19 cold regions 35 mm long). Reduction of the concn. of methyl violet in naphthalene from 10^{-3} to 10^{-6} g per g in one passage of this tube is reported. Analogies are drawn between the process of differential thermal analysis and distillation as a means of separating mixtures, and the establishment of a phase diagram for the system phenanthrene - anthracene is attempted as an illustration.
E. G. CUMMINS

Chromatography, ion exchange, electrophoresis

2687. **Simple automatic valve for constant-volume collection in column chromatography.** G. J. Nelson (Donner Lab. of Biophys. and Med. Phys., Univ. of Calif., Berkeley, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1724–1725.—The unit described, suitable for use with volumes in the range 1 to 20 ml, and capable of modification to take 100 ml, consists of a solenoid-operated Teflon valve. A 7° tapered ground glass seat is sealed into the lower end of a length of tubing (1 cm external diam.). The Teflon valve is machined to fit this taper and is opened electrically after the meniscus of the liquid collected above it interrupts the light falling on a photocell. A short time delay is employed to prevent double tripping, and to allow the turntable to move before the collected volume runs into the fresh tube. E. G. CUMMINS

2688. **Simple elution technique for paper chromatography.** G. K. Barashkov (Polar Res. Inst. of Fish Industry and Oceanography, Murmansk, USSR). *Lab. Delo*, 1960, **6** (6), 44–46.—The apparatus devised stands in a large desiccator. Two metal legs support a rectangular glass plate (2 cm wide) and a trough of the same length, but at a slightly higher level. The glass plate serves as a stand for miniature receiving flasks made from tubes 3·5 to 4 cm high. If the chromatogram has been spotted with the test soln., the spot is cut from a control so that it lies in the centre of an oval piece of filter-paper with two strips ($\lessdot$ 1·5 cm long) projecting from it at right angles. One strip dips into the trough containing eluent and the other strip dips into the receiving flask; the whole apparatus is then placed in the desiccator containing a little eluent, which serves to create the moist atmosphere necessary for rapid elution. The apparatus is modified slightly if the chromatogram zones are in the form of bands. The time required for complete elution is established by control tests with filter-paper pieces or bands of the appropriate size; for this purpose it is advisable to use test-tube chromatography. K. R. COOK

2689. **Device for automatic application of detection reagents to chromatographic paper.** M. Štefl (Chem. Dept., School of Agric., Prague). *Chem. Listy*, 1960, **54** (1), 1187–1189.—The device consists of a burette with numerous capillary apertures, 3 mm apart, for the flow of reagents. The chromatographic paper is moved under the capillaries so that the reagent soln. are mixed on the paper.
J. ZÝKA

2690. **Contribution to the study of centrifugal chromatography.** J. Dauphin, M. Maugarny, J. A. Berger and C. Dorier (Fac. Méd. et Pharm., Clermont-Ferrand, France). *Bull. Soc. Chim. France*, 1960, (11–12), 2110–2113.—This new technique is shown to effect the separation of certain dyes and of simple amino-acids. The apparatus consists essentially of a circular plate (diam. 40 cm) which carries the chromatographic paper horizontally and rotates

at 550 r.p.m. The plate is contained in a closed cylindrical box, the lid of which is provided with an aperture to permit the developing solvent to be sprayed on to the rotating paper near the centre. A device which gives close control of the rate of spray is described. The atmosphere of the container is kept saturated by means of soaked filter-paper placed in the bottom. Separations which normally require 16 to 24 hr. have been effected in 40 min. by centrifugal chromatography. Surface friction between the atmosphere and the paper causes evaporation by slight warming. The flow of liquid is thus affected by hydrostatic and centrifugal forces, and by capillary resistance and evaporation. A mathematical treatment of the movement of the solvent is given. J. R. HUDSON

2691. **Quantitative evaluation of paper chromatograms by direct photometry in u.v. light. Determination of sugars.** G. Jayme and H. Knolle (Inst. f. Cellulosechem. mit Holzforsch., Tech. Hochsch., Darmstadt, Germany). *Z. anal. Chem.*, 1960, **178** (2), 84–100 (in German).—The determination of pentoses and hexoses in paper pulp, after hydrolysis of the pulp and neutralisation on an ion exchanger, is described. After separation of the sugars on phosphate-impregnated paper to form a band chromatogram, the bands are detected with 2-aminobiphenyl - oxalic acid reagent and the paper is made transparent by treatment with methyl salicylate. The colours formed are measured at 380 mμ; standard curves are prepared for comparison. The influence of reaction time and the source of possible deviations from Beer's law are discussed. P. D. FARR-RICHARD

2692. **Instrument for the measurement of fluorescence of paper-chromatographic spots.** G. F. Bailey (West. Reg. Res. Lab., U.S. Dept. of Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1726–1727.—The instrument described by Semm and Fried (*cf. Naturwissenschaften*, 1952, **32**, 326) has been modified. Maximum collecting efficiency is attained with spots $\geq$ 38 mm in diameter, which is the size of the photocell aperture. Results obtained on calibration data for conversion of galvanometer readings to give the amount of fluorescing substance, namely coumestrol, yielded a standard deviation of $\simeq 7\%$ of the quantity measured ($\simeq 10^{-7}$ g). E. G. CUMMINS

2693. **Simple preparation of definite gaseous mixtures for calibration in gas-chromatographic analysis of traces of compounds.** J. Novák (Lab. Gas Analysis, Acad. Sci., Brno, Czechoslovakia). *Chem. Listy*, 1960, **54** (11), 1189–1193.—The procedure described is suitable for sampling and dilution of liquid and gaseous mixtures in concn. of 10^{-5} to 10^{-7} g per litre with the use of an injection syringe, and can be used for all methods of calibration, *e.g.*, by comparison of the heights or areas of chromatographic curves, by the method of standard addition, and by the method of internal standards. J. ZÝKA

2694. **High-temperature thermostat for gas chromatography.** E. H. Dubský (Lab. Gas Analysis, Acad. Sci., Brno, Czechoslovakia). *Chem. Listy*, 1960, **54** (11), 1183–1186.—A thermostat with a temp. range up to 550° was constructed with a two-step heating system; the first serves for the rough stabilisation of the temp., the second for a more precise control of temp. J. ZÝKA

2695. **Working properties of a high-temperature gas chromatograph with flame ionisation detector.** J. Novák, M. Rusek and J. Janák (Lab. Gas Analysis, Acad. Sci., Brno, Czechoslovakia). *Chem. Listy*, 1960, **54** (11), 1173–1183.—The construction and function of a gas-chromatographic apparatus are described. Examples are given of a wide range of applications, *e.g.*, for the determination of volatile compounds (formaldehyde, acetone, ether, methanol and ethanol) in blood, and for the determination of saturated and unsaturated hydrocarbons in gas for the analytical control of the production of coal tar, etc. The apparatus can be used for determining compounds in 10^{-9}M concn. J. ZÝKA

2696. **Optimum conditions for separation in gas chromatography.** J. C. Giddings (Univ. of Utah, Salt Lake City, U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1707–1711.—Optimum conditions have been derived from consideration of F, the separation function, which is defined as $(t_1 - t_2)^2/8(\tau_1^2 - \tau_2^2)$, where t_1 and t_2 are the retention times of two successive peaks and τ_1 and τ_2 are the respective standard deviations in time units (equal to one-fourth of the peak width). Optimum conditions derived or discussed for packed columns include column length, flow velocity, temperature, pressure and particle diameter. Those derived for capillary columns include flow velocity, pressure, temperature, tube diameter and thickness of liquid layer. E. G. CUMMINS

2697. **Minimisation of time in gas-chromatographic separations.** D. D. DeFord, B. O. Ayers and R. J. Loyd (Northwestern Univ., Evanston, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (12), 1711–1712.—An expression is given for the time required for elution of the ith component, in terms of the solute, the carrier gas and the column operating parameters. E. G. CUMMINS

2698. **Gas - liquid chromatography in capillary columns. I. Theory.** P. C. Haarhoff and V. Pretorius (Univ. Pretoria, S. Africa). *J. S. Afr. Chem. Inst.*, 1960, **13** (2), 97–115.—A rigorous mathematical treatment of gas - liquid chromatography in liquid-coated capillary columns is presented. The several parameters considered include carrier-gas velocity, concn. of solute, band width, time, and the shape of the elution curve. The ultimate efficiency of separation of a coated capillary column has been calculated. The equations are valid provided that the number of theoretical plates is large.

II. Factors affecting the column efficiency: the distribution coefficient, the diffusivity of the solute in the gaseous and liquid phases, and the thickness of the liquid layer. P. C. Haarhoff and V. Pretorius. *Ibid.*, 1960, **13** (2), 116–124.—Factors affecting the separation efficiency are discussed. It is shown that for high column efficiency there is an optimum thickness of the liquid layer, and that the ratio of the concn. of solute in the gaseous phase to that in the liquid phase at equilibrium, and the ratio of the diffusivity of the solute in the gaseous phase to that in the liquid phase should be very low. T. R. ANDREW

See also Abstracts—**2284**, Use of fused salts on glass-fibre strips. **2459**, Gas-chromatographic determination of H with hydrocarbons. **2657**, Use of *o*-phthalic - polyoxyethylene glycol polyester in gas chromatography of fatty acid esters.

Optical

2699. **X-ray structural analysis of radioactive samples.** Yu. I. Gribanov. U.S.S.R. Pat. 127,470 (25.3.60).—To remove the influence of the γ-radiation of the sample itself, the X-ray beam is modulated by a rotating perforated disc between the source and the sample, and the variable component of the signal reflected from the sample is separated in the receiver, *e.g.*, by a selective amplifier tuned to the frequency at which the X-ray beam is interrupted by the disc. C. D. KOPKIN

2700. **Use of a "singing" arc for the control of the process of feeding the substance into the d.c. arc plasma.** É. E. Vaĭnshteĭn, Yu. I. Belyaev and M. M. Farafonov (V. I. Vernadsky Inst. of Geochem. and Anal. Chem., Acad. of Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (5), 550–555.—This technique (*cf.* Belyaev and Vaĭnshteĭn, *Anal. Abstr.*, 1959, **6**, 4222) can be used to increase the reproducibility of spectrographic analysis. The duration of sound signals and pauses depends on the concn. and volatility of impurities evaporating on the electrode and on their ionisation potentials. These were investigated for a number of elements.
J. W. PRICE

2701. **The importance of extinction ratios in the spectrophotometric analysis of mixtures of two known absorbing substances.** A. L. Glenn (Sch. of Pharm., Univ. of London, Brunswick Square, London). *J. Pharm. Pharmacol.*, 1960, **12** (10), 595–608.—The accuracy of a two-point spectrophotometric assay depends on the establishment of numerical coeff. which apply to the analyst's own instrument at the time of analysis. It is necessary to determine absolute values of the extinction coeff. only for one component A at one wavelength λ_1 and for the other B at λ_2, since the other coeff. needed can be calculated from extinction ratios of soln. of pure A and pure B, respectively, measured in soln. of unknown concn. Simple criteria have been established to help the analyst to avoid pairs of wavelengths and concn. ratios that are unsatisfactory for precision, and a procedure for choosing the best values for λ_1 and λ_2 for a given pair of substances is described in detail. This new approach is of value in formulating a general procedure for the assay of injections which contain absorbing bacteriostats.
A. R. ROGERS

2702. **Calculation of the errors of an absorption analyser of gaseous or liquid mixtures.** A. O. Sall'. *Optics and Spectroscopy*, 1960, **8** (4), 301–302; English translation from *Optika i Spektroskopiya*, 1960, **8** (4).—The various errors that may arise when using a non-dispersive i.r. gas analyser are discussed and assessed. In addition to instrumental and calibration errors, attention is also given to the effects of changes in ambient temperature and atmospheric pressure. B. S. COOPER

2703. **Infra-red gas analyser.** Infra Red Development Co. Ltd. [Inventor: P. W. Walduck]. Brit. Pat. 857,598; date appl. 28.8.56.—In the detector chambers of typical i.r. gas analysers, mechanical shock or vibration may deflect the diaphragm and give rise to a false indication. To eliminate this source of error, a second diaphragm is provided, arranged parallel to the first, so as to be similarly affected by mechanical shock, and is made to contribute to the capacitance of the condenser, but is not subjected to any variation of pressure due to heating by the radiation. J. M. JACOBS

2704. **Pressed samples for infra-red spectrometry.** V. S. Akselrod. *Optics and Spectroscopy*, 1960, **8** (5), 379–380; English translation from *Optika i Spektroskopiya*, 1960, **8** (5).—An evacuable die for making alkali halide pressed-disc specimens is described. With this die, discs of high quality for i.r. spectroscopy are obtained with the following pressing schedule—pressure, 7 to 8×10^3 kg per sq. cm; evacuation time before pressing, 3 to 5 min. (to achieve a vacuum of 0·1 to 1 torr); time of pressure development to full load, 2 to 3 min.; and time of pressure release, 3 to 5 min. The mechanical residues from optical prism manufacture provide a satisfactory form of KBr for disc preparation.
B. S. COOPER

2705. **Potassium bromide discs for liquid samples.** R. E. Clark (E. I. du Pont de Nemours & Co. Inc., Wilmington, Del., U.S.A.). *Appl. Spectroscopy*, 1960, **14** (5), 139.—Cup-shaped potassium bromide pellets are suggested for forming expendable cells for samples containing water, odoriferous materials or liquids of high viscosity, which are ruinous to, or difficult to clean from, ordinary liquid cells.
P. T. BEALE

2706. **Contamination of potassium bromide pellets by plastic mixing vials.** N. T. McDevitt and W. L. Baun (Materials, Central, Wright-Patterson Air Force Base, Ohio, U.S.A.). *Appl. Spectroscopy*, 1960, **14** (5), 135–136.—The use of an expendable polystyrene vial, Plexiglas ball pestle and slip-on polyethylene lid for grinding and mixing potassium bromide pellets gives rise to spurious absorption bands which were found to be due to contamination resulting from abrasion of the various plastics used.
P. T. BEALE

2707. **The Essential Oil Association infra-red procedure: a prototype for industrial specification methods.** Essential Oil Association, Instrumental Analysis Subcommittee, Scientific Section (2, Lexington Ave., New York 10, N.Y.). *Appl. Spectroscopy*, 1960, **14** (5), 113–116.—Quantitative i.r. methods of analysis are defined in terms of six basic techniques, such as the use of a single beam when the unknown is in solution of a specified solvent or a double beam when the pure product, free from the component being determined, absorbs energy at the analytical wavelength. Specific operating conditions are required for the determination of individual oils and aromatics, and a typical example is given for the determination of hydroxycitronellal in hydroxycitronellal dimethyl acetal. All terms used are clearly defined.
P. T. BEALE

2708. **A burner for atomic absorption spectrophotometry.** O. E. Clinton (Rukuhia Soil Res. Sta., Dept. of Agric., Hamilton, N.Z.). *Spectrochim. Acta*, 1960, **16** (9), 985–988.—A water-cooled burner is described which gives a flame 12 cm long and approx. 4 cm high for use in atomic absorption spectroscopy. The effective flame path may be selected between 1 and 12 cm by rotating the burner with reference to a circular scale, in order to cover a 12-fold range in sensitivity.
P. T. BEALE

2709. **Method and apparatus for the photometric titration of solutions.** V. G. Zizin, Yu. N. Erastov, V. D. Il'in and L. M. Proskuryakov. U.S.S.R. Pat. 128,651 (15.5.60).—For the continuous titration of a flowing soln., soln. of indicator and buffer are

continuously mixed with the stream of test soln., and the mixed soln. is passed continuously through a cell consisting of a number of successive identical sections, the soln. passing through each section in turn. Each section is fed with a soln. of titrant from a common reservoir, so that the concn. of titrant increases regularly along the sections and, at the point where its concn. is equivalent to the substance being titrated, the colour and extinction of the soln. differ from those in the preceding sections. A similar sectional cell not fed with titrant is used as comparison cell. The apparatus is illustrated. C. D. KOPKIN

2710. **New or improved instrument for measuring the fat content of skimmed milk.** Dairy Supply Co. Ltd. [Inventor: F. K. F. Goodman]. Brit. Pat. 857,954; date appl. 19.8.58.—The instrument comprises a hollow cylindrical body having in line, on its longitudinal axis, an observation eye-piece, a marked ground-glass screen illuminated from the rear by an electric lamp, and a cell to hold the milk to be tested. The cell is defined by transparent walls which are relatively adjustable to vary their separation, and hence to vary the thickness of the layers of milk between them. The device is calibrated in terms of fat content by setting it so that the markings on the screen are just visible through the eye-piece when layers of milk having different known fat contents are in the cell. J. M. JACOBS

2711. **A practical temperature-compensated hand refractometer (the TS meter), its clinical use and application in estimation of total serum proteins.** K. G. Barry, A. W. McLaurin and B. L. Parnell. *J. Lab. Clin. Med.*, 1960, **55** (5), 803–808.—From a study of the practical performance of a commercial (U.S.) refractometer it is concluded that the instrument gives rapid, reproducible results on human serum (1 drop), and that a statistically reliable estimate of total serum proteins may be made from the readings for total serum solids. W. H. C. SHAW

2712. **A single-beam optical-acoustic gas analyser.** M. L. Veingerov and A. A. Sivkov. *Optics and Spectroscopy*, 1960, **8** (5), 388; English translation from *Optika i Spektroskopiya*, 1960, **8** (5).—Most non-dispersive i.r. gas analysers are based on the double-beam principle, or employ a single-beam two-channel scheme. The instrument described, which incorporates a well-stabilised, linear amplifier, achieves good sensitivity and accuracy with a single-beam single-channel system. Instead of a signal obtained from the second comparison channel of a normal gas analyser, a voltage from an auxiliary stabilised source is used, arranged to be equal and opposite in sign to the output of the amplifier when there is no gas under examination in the absorption cell. B. S. COOPER

See also Abstracts—**2269**, Combined estimates in colorimetry. **2280**, NH_4HSO_4 as fusion agent in spectography. **2341**, Pulse generators for excitation of spectra.

Electrical

2713. **Dissolution of a platinum anode during electrolysis with a mercury cathode.** Shizo Hirano, Atsushi Mizuike and Masao Saeki (Inst. Tech.-anal. Chem., Fac. of Engng, Tokyo Univ., Hongo, Tokyo). *Japan Analyst*, 1959, **8** (12), 827–828.—The amount of Pt which dissolves in the mercury cathode is $\simeq 10$ μg in 3 hr. at 7° (2 V, 6 amp.) in N-H_2SO_4 electrolyte and 50 to 80 μg in 6 hr. at 16° (2 V, 7 amp.). The Pt appears to be the source of the blank value in colorimetry with nitroso-R salt. K. SAITO

2714. **Moisture-content-indicating apparatus.** R. Legg Ltd. and P. Q. R. Schreiber. Brit. Pat. 858,281; date appl. 24.4.56.—Portions of a moving web or band of material, the moisture content of which is to be indicated, *e.g.*, cut tobacco or cereals, are compressed successively to a controlled degree and brought into contact with a pair of electrodes so as to close an electrical circuit and generate pulses of current, the amplitude of which is determined by the moisture content of the material. These pulses are then integrated and the integrated signal, which is determined by the average value of the moisture content of the material, is fed to a suitable indicating apparatus. J. M. JACOBS

2715. **Improvements in and relating to methods of and apparatus for measuring the concentration of oxygen dissolved in liquid [particularly boiler feed water].** Cambridge Instrument Co. Ltd. [Inventor: G. Jessop]. Brit. Pat. 858,677; date appl. 20.12.57.—A stream of hydrogen is circulated through a scrubbing vessel into which the oxygen-containing liquid under test is passed and where the oxygen is extracted. The resulting oxygen-containing hydrogen is passed through an electrochemical measuring cell (a vessel containing a hydrogen-saturated soln. of an electrolyte, a cathode and an anode consisting of a platinum wire coated with platinum black) which generates a signal indicative of the oxygen concn. in the liquid under test. The hydrogen is generated in a cell by electrolysis of, *e.g.*, a soln. of KOH, and is passed through a furnace containing a catalyst, *e.g.*, palladised asbestos, so that any oxygen in the gas generated by the cell is caused to combine with hydrogen to form water vapour. J. M. JACOBS

2716. **Polarographic investigations in non-aqueous solvents.** G. Schöber and V. Gutmann (Inst. für anorg. und allg. Chem., Tech. Hochsch., Wien, Austria). *Z. Elektrochem.*, 1959, **63**, 274.—Polarographic measurements were made *vs.* the N.C.E. in non-aq. ethylenediamine, benzoyl chloride, acetic anhydride, morpholine and phosphoryl chloride. The half-wave potentials in these solvents are completely different from those of aq. soln. Anomalies are found in the curves. Ions such as Ca^{2+} and Mg^{2+}, which cannot or can only with great difficulty be determined in water, give well-defined curves in non-aq. ethylenediamine and in acetic anhydride. J. ELECTROANAL. CHEM. ABSTR.

2717. **Differential electronic polarograph.** Yu. V. Gorelkinskii, I. G. Grinman and G. S. Kozlov (Inst. of Nuclear Physics, Acad. Sci., Kazakh SSR). *Zavod. Lab.*, 1960, **26** (9), 1141–1143.—An apparatus in which the Faraday and capacity currents are separated by use of a phase-sensitive bridge is described. G. S. SMITH

2718. **Use of fixed mercury electrodes in oscillographic polarography.** Ya. P. Gokhshtein (V. I. Vernadsky Inst. of Geochem. and Anal. Chem., Acad. of Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (5), 541–549.—Conditions for the anodic oscillographic polarography of Cd^{2+}, Pb^{2+} and In^{3+} in N-HCl, Nb^{V} plus Ti in 23N-H_2SO_4, and U^{VI} in

N-HNO_3 were established by using fixed mercury electrodes. The method was then applied to the automatic control of industrial effluents by the use of a special flow cell. Deoxygenation is unnecessary, and high sensitivity, selectivity and reproducibility can be attained. J. W. PRICE

2719. **Resin membranes as indicator electrodes in acid - base titrations.** R. Geyer and P. Niklas (Inst. f. anal. Chem., Tech. Hochsch. Chem., Leuna-Merseburg, Germany). *Z. anal. Chem.*, 1960, **177** (3), 166–175 (in German).—Details are given for the preparation of synthetic membranes (*e.g.*, of phenol - formaldehyde, phenolsulphonic acid - formaldehyde, salicylic acid - resorcinol - formaldehyde, and anthranilic acid - resorcinol - formaldehyde resins), and their application as indicator electrodes has been studied. The membranes are cemented to glass tubes with a synthetic resin (Phthalopal G). It is shown that the membranes containing anthranilic acid are suitable for acid - base titrations, and typical curves obtained by using the polarised system of Reilley *et al.* (*cf. Anal. Chem.*, 1951, **23**, 1233) are presented.
B. B. BAUMINGER

2720. **Automatic titrator working on the principle of the second derivative.** W. Wiessner, D. Kandler and W. Beckert (Res. Inst. Non-Ferrous Metals, Freiberg/Sax., Germany). *Acta Imeko*, 1959, **4**, 414.—The end-point of potentiometric titrations can be determined from the potential value corresponding to the end-point, or from the zero value of the second differential quotient of the function expressing the relation between the electrode potential and the volume of titrant. These two possibilities are compared and the brief theory of the second one is given. The differentiation is achieved by RC members. Using a push-pull switch it is found that the instrument is equally well suited for the measurement of either increasing or decreasing potential curves. The time needed for the titration can be reduced to 40 sec.
J. ELECTROANAL. CHEM. ABSTR.

2721. **Improvements in and relating to the determination and control of compositions in chemical processes by titration.** Imperial Chemical Industries Ltd. [Inventors: J. F. Brown, R. J. Weir and A. R. Whelan]. Brit. Pat. 855,708; date appl. 27.2.56.—A sample of solution, automatically pipetted from a bulk or stream of liquid, is automatically titrated to a desired chemical end-point or pH value by filling a burette, which has a liquid-level finder, with a standard solution, titrating the sample with the standard solution with constant stirring, the rate of addition of the standard solution being decreased towards the end of the titration, which is indicated by an end-point detector in the titrating zone, and recording the amount of standard solution used. The automaticity of these operations is effected by means of a sequencing switch, having a number of configurations for bringing into play, as required, electrical circuits operating valves controlling flow into and from the burettes and flow from the titrating zone, and driven by a relay. The driving of the sequencing switch is initiated by timed electrical signals originating from the liquid-level detectors in the burette(s), or titrating zone or from the end-point detector. The decrease in the rate of addition of the standard solution is effected at a pre-determined stage of titration by a combination of anticipating, trigger and time-delay sub-circuits. J. M. JACOBS

2722. **Amperometric titration by solutions of sodium pentamethylenedithiocarbamate.** Yu. I. Usatenko and K. A. Uvarova (F. É. Dzerzhinskii Dniepropetrovsk Chem.-Tech. Inst.). *Zavod. Lab.*, 1960, **26** (10), 1098–1101.—At an applied potential of +0·9 V *vs.* the S.C.E., Cu, Pb, Cd and Ag can be titrated amperometrically with 0·01M or 0·005M-Na pentamethylenedithiocarbamate.
G. S. SMITH

2723. **Voltammetry at inert electrodes. I. Analytical applications of boron carbide electrodes.** T. R. Mueller and R. N. Adams (Univ. of Kansas, Lawrence, U.S.A.). *Anal. Chim. Acta*, 1960, **23** (5), 467–479 (in English).—The construction of boron carbide electrodes is described and an account is given of their behaviour in 22 different polarographic applications involving both oxidation and reduction of inorganic and organic species. The boron carbide electrode functions as an "inert" electrode. In general, residual currents are small, and half-peak potentials are reproducible and agree with literature data within a few mV. Peak currents can be measured with a precision of $\simeq 1\%$.
H. N. S.

2724. **Remote-handling and analytical techniques used in the processing of samples from H.T.G.C. loop irradiations.** P. E. Brown, R. H. Flowers and D. F. M. Lupton (A.E.R.E., Harwell, Berks., England). A.E.R.E. Report AERE–R3252, 1960. 20 pp.—The cell used and its operation are described and illustrated; it is constructed of lead and concrete and internally is 12 ft. 6 in. high, 10 ft. wide and 6 ft. deep. A working table (8 ft. × 4 ft.) is fitted inside the cell. It is equipped with master-slave manipulators and up to about 200 C of mixed fission products may be handled. The radiochemical procedures refer to the examination of UC - graphite compacts, charcoal, soda lime, and stainless steel for fission products.
G. J. HUNTER

2725. **Electron-probe X-ray micro-analyser: an important micro-analytical tool.** R. Kiessling (Swedish Inst. for Metal Res., Stockholm). *Jernkontor. Ann.*, 1960, **144** (11), 847–854.—The principles and main correction factors for electron-probe X-ray micro-analysis are given. The Cameca instrument is described. Future trends and other electron-probe instruments are discussed and examples of the application of the technique are given. P. PEDERSEN

2726. **Indirect neutron absorptiometry.** W. W. Meinke (Michigan. Univ., Ann Arbor). *U.S. Atomic Energy Comm.*, Report TID-6325, 1957. 5 pp.—The investigation of neutron absorption for use in the determination of common elements such as fluorine is discussed. Preliminary results indicate that indirect neutron absorptiometry is satisfactory, and that values reproducible to within a few per cent. can be rapidly obtained by this technique. The method should also be applicable to ions other than fluoride that form insoluble compounds with Gd. NUCL. SCI. ABSTR.

2727. **Apparatus for studying nuclear magnetic resonance in solids.** J. J. Capart, P. Loosen and M. Van Meerssche (Phys. Chem. Lab., Univ. Louvain, Belgium). *Bull. Soc. Chim. Belg.*, 1960, **69** (5–6), 292–302.—In the apparatus described, the transmitter and receiver are connected by a high-frequency bridge, in one arm of which is the coil

surrounding the sample. A battery-powered electromagnet provides a field of 5000 gauss. The resonance signal, after amplication, is fed into a phase detector, which produces a derivative signal and also raises the signal to noise ratio.

J. H. WATON

2728. **Small general-purpose double-focusing mass spectrometer.** A. O. Nier (Univ. Minnesota, Minneapolis, U.S.A.). *Rev. Sci. Instrum.*, 1960, **31** (10), 1127–1132.—A small light-weight mass spectrometer incorporating a 90° electrostatic analyser and a 60° magnetic analyser is described. The radius of curvature of the ion path in the magnetic analyser is 2 in. Sensitivity and resolution are comparable with those of larger conventional instruments, while the small size and weight make it suitable for rocket and satellite investigations. G. SKIRROW

2729. **Improvements to a mass spectrometer for organic structure analysis.** R. Ryhage (Lab. for Mass Spectrometry, Kem. Inst. I, Karolinska Inst., Stockholm, Sweden). *Arkh. Kemi.*, 1960, **16** (1–2), 19–49.—Modifications and improvements to a mass spectrometer are described. Constructional details of the ion source, analyser tube and collector, and circuit diagrams for the electronic systems of the instrument, are given in full.

C. A. SLATER

2730. **Low-background tungsten filaments for surface-ionisation mass spectroscopy.** J. W. Frazer, R. P. Burns and G. W. Barton (Radiation Lab., California Univ., Livermore, U.S.A.). *Rev. Sci. Instrum.*, 1959, **30** (5), 370–371.—Unusual background peaks occur in high-sensitivity solid-sample mass spectroscopy when using a multiple-filament surface-ionisation source. These have been identified as being due to polymeric ions of K, which is normally present as an impurity in the tungsten filament. A technique is described for the production of a K-free tungsten filament by deposition from $W(CO)_6$ vapour on to a tantalum former, which is then volitalised away. When this is used in a mass spectrometer, capable of measuring < 100 $\mu\mu$g of U, background in the mass region 230 to 245 has been eliminated.

P. T. BEALE

2731. **Improvements in or relating to mass spectrometers [for determining the ratio of the concentrations of two constituents of a gas mixture].** Philips Electrical Industries, Ltd. Brit. Pat. 857,001; date appl. 22.2.57. Netherlands, date appl. 27.2.56.—The ratio of the concn. of the two constituents is indicated by a comparison between the heights of two mass peaks. Shortly before each periodic change of the accelerating voltage, the ion flow is interrupted and, after a certain period of time, is restored again, so that an interrupted sequence of square-wave output voltages is produced. These output voltages are supplied to a change-over device which operates in synchronism with the periodic changes, two capacitors being charged through this device to the mean voltages of the alternating voltage waves which correspond to the constituents of the mixture. The periodic interruption of the ion stream ensures that no mass peaks can occur that correspond to constituents of the mixture, the mass peaks of which lie between those of the constituents, the concn. ratio of which is to be ascertained. J. M. JACOBS

See also Abstracts—**2272**, Purification of tetrabutylammonium iodide for polarography. **2323**, Electrode for Al in fused cryolite. **2350**, PbI_2 for mass spectrometry. **2397**, Ion counting in mass spectrometry. **2572**, Interpretation of polarographic waves.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
Colour Index	C.I.
concentrated	conc.
concentration	concn.
constant	const.
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
equivalent	equiv.
ethylenediaminetetra-acetic acid	EDTA
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_l
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_B
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

The chemical nomenclature used in the abstracts is that recommended by The Chemical Society ("Handbook for Chemical Society Authors", The Chemical Society, London, 1960), and may differ from that used in the original articles.

Volume 8. No. 6, Abstracts 2264–2731 June, 1961

ANALYTICAL ABSTRACTS

A PUBLICATION OF
THE SOCIETY FOR ANALYTICAL CHEMISTRY

EDITORIAL COMMITTEE

Chairman: B. A. Ellis

Members: B. S. Cooper, C. H. R. Gentry, C. A. Johnson, H. F. W. Kirkpatrick, B. J. Walby, W. A. Waygood, K. A. Williams
and
President of the Society: A. J. Amos

Hon. Secretary of the Society
R. E. Stuckey

Hon. Treasurer of the Society
D. T. Lewis

Editor: Norman Evers, B.Sc., Ph.D., F.R.I.C.

Assistant Editor: Mrs. H. I. Fisk, B.Sc.

CONTENTS

	Abstract
General Analytical Chemistry	
Reviews; reagents; methods of general application	2264
Inorganic Analysis	
General methods; elements (in order of the Periodic Table); minerals; industrial products	2284
Organic Analysis	
Elements and radicals; organic compounds; industrial products	2448
Biochemistry	
BIOLOGICAL FLUIDS; ANIMAL AND VEGETABLE TISSUES	2538
PHARMACEUTICAL ANALYSIS	2600
FOOD	
Food additives; beverages; edible oils and fats; vitamins	2633
SANITATION	
Air; water; sewage; industrial wastes	2661
AGRICULTURAL ANALYSIS	
Soil; fertilisers; herbicides; pesticides; animal feeding-stuffs	2666
General Technique and Apparatus	
GENERAL	2677
CHROMATOGRAPHY; ION EXCHANGE; ELECTROPHORESIS	2687
OPTICAL	2699
ELECTRICAL	2713

Printed and published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England
Communications to be addressed to the Editor, Norman Evers, 14, Belgrave Square, London, S.W.1.
Enquiries about advertisements should be addressed to Walter Judd Ltd., 47, Gresham Street, London, E.C.2.
Entered as Second Class at New York, U.S.A., Post Office.